Energy Research and Development Division

FINAL PROJECT REPORT

Trevi Systems' Forward Osmosis Pilot at Orange County Water District

California Energy Commission

Gavin Newsom, Governor

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PREPARED BY:

Primary Author(s):
Sophie Mancuso
Gary Carmignani
John Webley

Trevi Systems
1415 N. McDowell Blvd, Suite A
Petaluma, CA 94954
Phone: 707-792-2681 | Fax: 707-792-2684
www.trevisystems.com

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PREPARED FOR:
California Energy Commission

Anish Gautam
Project Manager

Virginia Lew
Office Manager
Energy Efficiency Research Office

Laurie ten Hope
Deputy Director
ENERGY RESEARCH AND DEVELOPMENT DIVISION

Drew Bohan
Executive Director

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The California Energy Commission is invaluable for startups such as Trevi Systems. It provides a necessary source of funding to scale up from pilot scale to commercial systems, as well as a level of credibility useful to seek partnerships.

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Toyobo provided many free membrane samples throughout this project. For that, the team is very thankful.

Thank you to the Trevi Team that worked on this project:

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PREFACE

The California Energy Commission's Energy Research and Development Division supports energy research and development programs to spur innovation in energy efficiency, renewable energy and advanced clean generation, energy-related environmental protection, energy transmission and distribution, and transportation.

In 2012, the Electric Program Investment Charge (EPIC) was established by the California Public Utilities Commission to fund public investments in research to create and advance new energy solution, foster regional innovation and bring ideas from the lab to the marketplace. The California Energy Commission and the state's three largest investor-owned utilities – Pacific Gas and Electric Company, San Diego Gas & Electric Company, and Southern California Edison Company – were selected to administer the EPIC funds and advance novel technologies, tools, and strategies that provide benefits to their electric ratepayers.

The Energy Commission is committed to ensuring public participation in its research and development programs that promote greater reliability, lower costs, and increase safety for the California electric ratepayer and include:

- Providing societal benefits.
- Reducing greenhouse gas emission in the electricity sector at the lowest possible cost.
- Supporting California's loading order to meet energy needs first with energy efficiency and demand response, next with renewable energy (distributed generation and utility scale), and finally with clean, conventional electricity supply.
- Supporting low-emission vehicles and transportation.
- Providing economic development.
- Using ratepayer funds efficiently.

Trevi System's Forward Osmosis Pilot at Orange County Water District is the final report for the Forward Osmosis Desalination of Industrial Waste Water project (Grant Number PIR-13-009) conducted by Trevi Systems. The information from this project contributes to the Energy Research and Development Division's EPIC program..

For more information about the Energy Research and Development Division, please visit the Energy Commission's website at www.energy.ca.gov/research/ or contact the Energy Commission at 916-327-1551.

ABSTRACT

Forward osmosis is an emerging desalination technology for producing fresh water that is less fouling (clogging) than reverse osmosis while requiring less energy for its operation. This technology can be used on more challenging water supplies, such as the waste stream of a reverse osmosis process. In forward osmosis, the water to be treated (feed solution) is drawn across a semipermeable membrane with a draw solution (a higher concentration solution than the feed solution) circulating on the clean water side. The draw solution draws or pulls clean water from the feed solution into the draw solution using osmotic pressure as the driving force. Trevi System's forward osmosis technology uses a draw solution that can be separated with heat instead of using electricity, which can be very advantageous when waste heat is available. Trevi conducted forward osmosis pilot tests on reverse osmosis (which uses high pressure pumps to force the feed solution through semi-permeable membranes) concentrate at the Orange County Water District for two-and-one-half years under various conditions. This project assessed the feasibility and performance of using forward osmosis to extract more water from the already-concentrated reverse osmosis waste stream.

Keywords: Forward osmosis, pilot, OCWD, fouling, membrane, Trevi Systems

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EXECUTIVE SUMMARY

Introduction

Trevi Systems is a California-based startup company specializing in developing forward osmosis technologies. Reverse osmosis is a process where high pressure pumps push feedwater across a semipermeable membrane that allow water molecules to pass through but no other compounds such as salts or organics. Electricity is needed to power the high pressure pumps. Unlike reverse osmosis, forward osmosis is a membrane technology used for treatment or desalination of water or both. In forward osmosis, the water to be treated (feed solution) is drawn across a semipermeable membrane with a draw solution (a higher concentration solution than the feed solution) circulating on the clean water side. The draw solution draws or pulls clean water from the feed solution into the draw solution using osmotic pressure as the driving force. The product water and draw solution are then separated in a second step. Forward osmosis is touted for having lower membrane fouling (clogging) potential than reverse osmosis while using significantly less electricity in the process.

Trevi Systems has developed a proprietary draw solution that can be separated from the product water with heat instead of using electrically-powered high pressure pumps. This technology is advantageous in settings where waste heat is available, since only a fraction of the electricity for seawater desalination is required. Trevi's forward osmosis has been piloted for seawater desalination in Kuwait, the United Arab Emirates, Japan, Saudi Arabia, and the United States.

Project Purpose and Process

When using reverse osmosis to clean wastewater, two streams are created, the desired clean water stream and a waste stream that contains everything that was separated from the clean water. This waste stream is called the *concentrate* and usually must be disposed of. The ratio of clean water compared to initial feed water is called *recovery*. Higher recovery is preferable because it means that more water (a higher percentage of the feed) is purified for reuse however, this typically creates operational challenges such as greater membrane fouling. Because forward osmosis has lower membrane fouling potential, this technology can be used to treat challenging waters, such as the concentrate produced from reverse osmosis treatment of tertiary-treated wastewater. Tertiary treatment is the final cleaning process that improves wastewater quality before it is reused, recycled, or discharged to the environment. With the potential for less fouling, forward osmosis could be used to increase overall water recovery of a facility. One such facility is the Groundwater Replenishment System at the Orange County Water District, a world leader in indirect potable reuse.

The Orange County Water District wants to increase water production of their Groundwater Replenishment System potable reuse facility beyond the current 100 million gallons per day and is exploring options including (1) expansion of the system by sourcing additional wastewater (supply), and (2) further concentration of the reverse osmosis concentration to recover more water. Other water resources outside reuse could be pursued, such as purchasing additional imported water, seawater desalination, groundwater banking arrangements, and so forth.

In 2013, the California Energy Commission offered a grant geared toward projects that use emerging technologies to save natural gas in the water sector. Trevi Systems received the grant to build and operate a 100 cubic meter per day forward osmosis pilot system at the Orange County Water District, to accelerate the path towards a commercial system. The goal of the project was to assess the feasibility and performance of using forward osmosis to extract additional water from the Groundwater Replenishment System tertiary reverse osmosis concentrate stream.

Because of the challenging nature of this type of feed water, small laboratory experiments were performed first on synthetically water made to mimic the chemistry of the reverse osmosis concentrate. The research team observed fouling of the membrane modules under certain conditions. Because a full characterization of the type of silica and organic matter present in the reverse-osmosis concentrate was not available, and because this affects the fouling behavior drastically, the project team decided first to design, build, and deploy a small pilot system in the field to test fouling of the membrane modules before proceeding with a full-scale demonstration project. The results of the small pilot test would guide the final design of the 100 cubic meter—per-day system.

Toyobo is one of the few membrane manufacturers in the world to produce reverse osmosis membranes with hollow fiber geometry, and the company was interested in expanding its membrane business to forward osmosis. In partnership with Trevi Systems, Toyobo worked on adapting its reverse osmosis membrane modules to forward osmosis. Trevi provided mini-modules to research the effectiveness of different configurations; some are already available in commercial sizes.

Project Results

After testing the traditional enclosed modules at the water district for 2.5 years, the project team realized that without pretreatment, these membrane modules were fouling quickly. The immersed type of module manufactured by Toyobo showed much more promise. However, Toyobo was not able to provide this type of module in quantities necessary for the 100 cubic meter per day system within this project so this module type was not tested. Three types of pretreatment were tested; high pH precipitation with acid addition; ion exchange resins; and a specialty membrane pretreatment. Pretreatment successfully decreased the concentration of fouling species in the feed water. All pretreatment options, however, required more chemicals than were considered feasible by district operations staff for use in a full-scale facility treating 10- to 20-million gallons per day of wastewater. Chemical pretreatment of reverse osmosis concentrate before membrane-based water extraction could potentially be feasible at other, smaller-scale facilities. The Orange County Water District is unique in that the Groundwater Replenishment System reuse facility is the largest of its kind in the world.

At the time of this project, Toyobo was only company able to produce hollow fiber modules with a small internal diameter. Because the Trevi Systems draw solution was more viscous than water, the project team switched the draw solution to a salt solution to continue the testing.

In addition, this was a new type of module and Toyobo would require time to assemble full-scale modules, so the team designed, built, and used a medium-scale system instead to experiment with up to four of the 3-inch diameter modules. The new medium-scale module design allowed operation without any pretreatment– a positive finding and a major benefit to any full-scale project. Data were collected to examine the tradeoff between membrane recovery and cleaning frequency that is, achieving higher recoveries that increased fouling and, therefore, required more cleaning. The fibers used in forward osmosis installations are typically woven and enclosed in a module giving them extra structure because of the closed geometry. The membrane fibers from the manufacturer were not strong enough to be adapted to this new open (non-woven fibers) module.

When testing at small scale to gather data, the project team could accommodate periodic fiber breakage. Broken modules were replaced, and instruments on the draw side were cleaned. These modules were not designed to be exposed to feed water compounds that build deposits. However, it was not practical to go to a larger scale, (including piloting) or full scale with these fragile membranes.

Parallel to this grant, Trevi Systems is developing its own hollow fibers membranes from a material that renders them strong and pH- and chlorine-resistant. The new hollow fiber membranes appear promising, and the research team must to put them in an immersed module form. After completing that task, the team plans to test the new membrane modules in the laboratory before testing them in the field.

Even though the team did not construct the 100-cubic meter per day system they found issues with the Trevi forward osmosis system at a small scale, and solutions that would not have been possible without piloting the system using real water. Based on the information gained, Trevi Systems has a clear path to a system that will work well on the type of water Orange County Water District provided: reverse osmosis concentrate for water reuse applications

Benefits to California

Ultimately, when Trevi Systems' forward osmosis technology is available at commercial scale, it will create an extra source of water for potable use, which is crucial to water treatment facilities. It also provides more autonomy to local water districts that rely on imported water as part of their portfolio

CHAPTER 1: Introduction

Trevi Systems

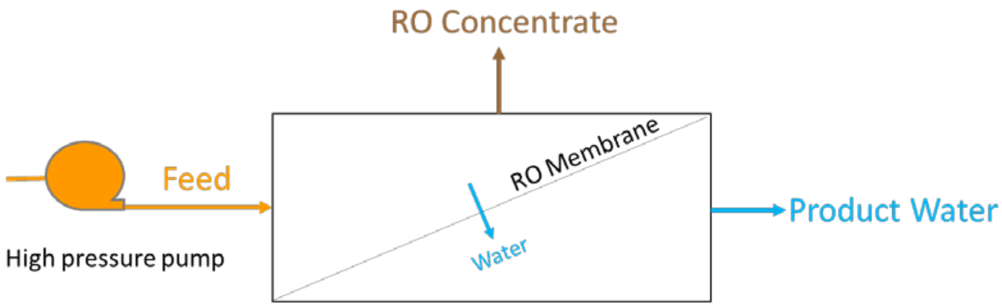
Trevi Systems is a California-based startup founded in 2010 with the goal of developing forward osmosis (FO) technology for water desalination. Trevi has developed a thermos(heat)responsive draw solution that is used in its FO process for seawater desalination by using waste heat and the thermosresponsive draw solution, Trevi's process uses less electricity than reverse osmosis. Trevi has also been developing membranes and other innovative water desalination technologies.

In 2013, Trevi conducted the first pilot test of its new FO technology at the United States Navy's Seawater Desalination Test Facility in Port Hueneme (Ventura County) to demonstrate the electrical and thermal energy requirements and to compare these energy requirements to those associated with seawater desalination using reverse osmosis (RO). Since then, Trevi has conducted pilot projects of increasing sizes in the United States, Kuwait, United Arab Emirates, and Japan to demonstrate the performance capabilities of the system. The project sponsored by this grant is a key part of that strategy since it was the first time the Trevi FO technology was tested on brackish RO brine.

Forward Osmosis Basics

In RO, pressure is applied to the feed water to push water across a semipermeable membrane that allows water molecules through but no other compounds such as salts or organics (Figure 1). Therefore, clean water is obtained on the other side of the membrane. RO requires large amounts of electricity to pressurize the feed. The amount of pressure required is proportional to the feed salt concentration and the desired water recovery. Pressure exchangers can be used to recover a portion of that energy.

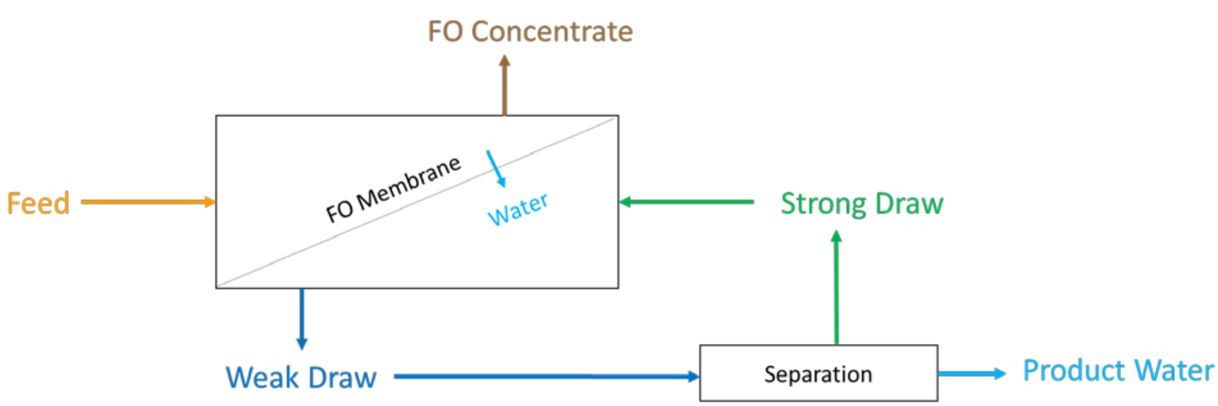
Figure 1: Diagram of Reverse Osmosis



Source: Trevi Systems

In FO, the osmotic pressure from the draw solution draws the water across the membrane, thereby eliminating the need for pressurizing the feed (Figure 2). The driving force is the osmotic pressure difference between the feed side and the draw side. Osmotic pressure can be defined as the force that a dissolved substance exerts on a semipermeable membrane, through which it cannot penetrate, when separated by it from pure solvent.[1] Water crosses the membrane toward the stronger osmotic pressure side (the draw). Water flows (fluxes) across the membrane and dilutes the draw. The draw must be separated from the product water and can be reused in closed loop within the FO system.

Figure 2: Diagram of a Generic FO System



Source: Trevi Systems

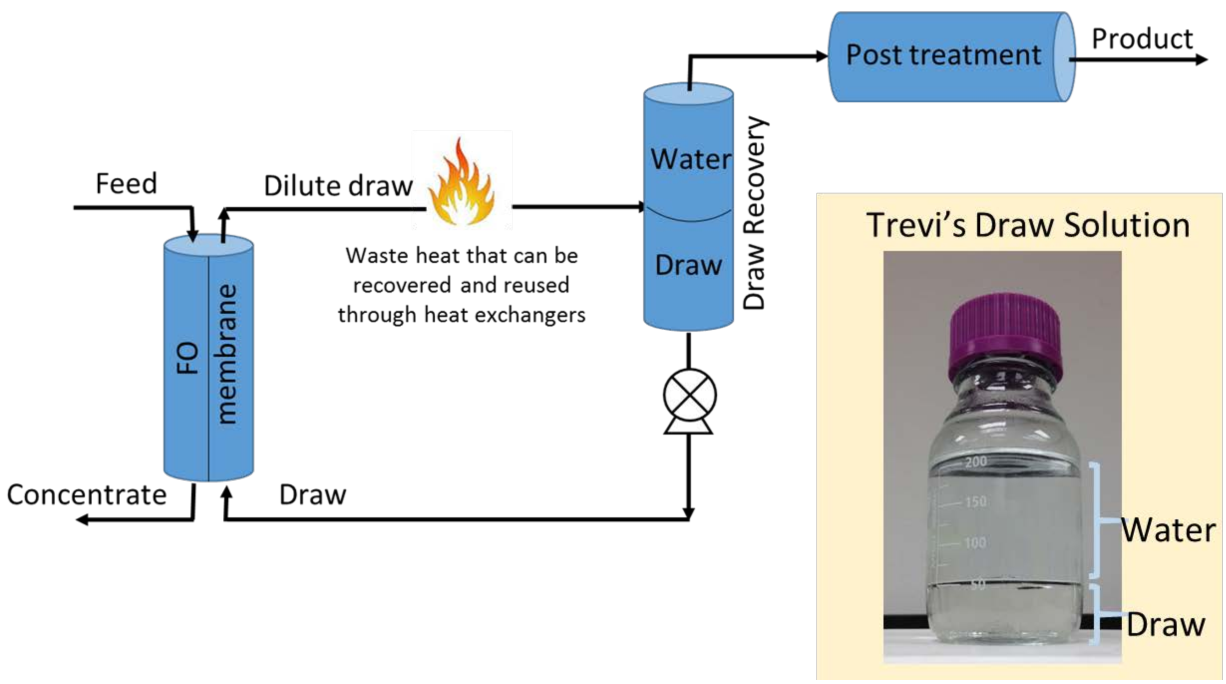
An advantage of FO is that it is more scaling-resistant than RO and that when fouling does occur, it is easier to clean. That allows the FO process to be used on challenging feed waters. One such example is the RO concentrate (ROC) of tertiary-treated wastewater. FO could be used to increase the overall water recovery of a tertiary treatment facility using RO. A world leader in indirect potable reuse is the Orange County Water District (OCWD) in Southern California.

1 http://www.dictionary.com/browse/osmotic-pressure.

Trevi's Forward Osmosis Technology

Trevi Systems developed a proprietary draw solution that is thermally responsive. When heat is applied to the draw-water solution, it separates into a concentrated draw solution that can be reused (it is circulated in a closed loop within the system) and product water (Figure 3). Because Trevi's FO technology does not require water to undergo a phase change (such as evaporation), it requires only a fraction of the heat necessary in multi-effect evaporation, multi-flash distillation, vapor compression, etc. The amount of energy required for FO is independent of feed concentration or recovery. Therefore, there must be a minimum feed salt concentration and recovery to be energetically advantageous compared to RO. Trevi System's FO has the potential to foul less than RO and to require less electricity.

Figure 3: Trevi System's Forward Osmosis Scheme



Source: Trevi Systems

The Groundwater Replenishment System at Orange County Water District

The OCWD provides water to 2.4 million people in Orange County by supplementing natural groundwater. One way the district supplements water is to reuse wastewater for potable application through groundwater recharge, considered "indirect" potable reuse due to the storage time in the natural groundwater aquifer. OCWD is a world leader in the water industry, especially in the indirect potable reuse of water. The Groundwater Replenishment System (GWRS) takes secondary treated municipal wastewater from the Orange County Sanitation District, located adjacent to OCWD, and treats it with a triple barrier of state-of-the-art technologies: microfiltration to remove bacteria, cysts, and large particles; RO to remove salts and most chemicals (pharmaceuticals, pesticides, etc.); and ultraviolet advanced oxidation, which irradiates and oxidizes organics that could have made it through RO. Finally, with the advanced treated, purified water is injected into the ground, where it travels for at least six months before reaching a drinking water well.

When using RO to clean water, two streams are created: the desired clean water and a waste stream that contains everything that was separated from the clean water. This waste stream is called the reverse osmosis concentrate (ROC). The ratio of clean water compared to initial feed water is called *recovery*. Higher recovery is preferable because it means that more water (a higher percentage of the feed) is purified for reuse, but it typically comes at a cost: greater membrane fouling and therefore operational challenges. The recovery at OCWD is 85%, which means that out of the roughly 100 million gallons per day (mgd) of water produced, 15 mgd end up as a waste stream. If it could extract more water out of that waste stream, the district would have more water to send to its users and save energy relative to costs of importing water from other locations, as this ROC wastewater source is already available on-site, particularly if minimal energy was necessary for the extraction (Figure 4).

OCWD was an ideal test site for this project because (1) OCWD is interested in testing emerging technologies, (2) OCWD has a reputation for environmental stewardship, and (3) the ROC feed water is a more challenging water to treat, allowing the research team to test the limits of the low-fouling reputation of FO.

Figure 4: Diagram of Forward Osmosis Use to Treat RO Concentrate and Increase the Overall Recovery of the GWRS

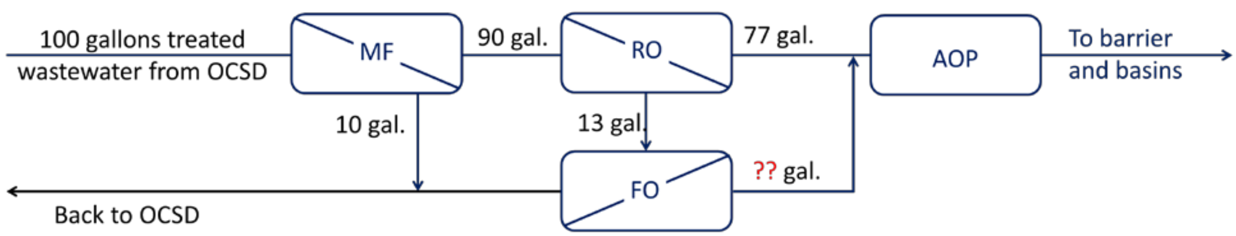


Figure legend: MF= microfiltration (90% recovery); RO = reverse osmosis (85%recovery), FO = forward osmosis, AOP = advanced oxidative process. RO is 85% recovery

Source: Trevi Systems

Grant Goals and Objectives

The goals of the grant were to design, build, and operate over the long term a 100 m^3/day FO R&D system to determine what the fouling properties and advantages FO might have over RO, particularly in the pre-treatment stage when used to extract more water from ROC. The test site was the GWRS facility at the OCWD. Other objectives included gaining further experience in operating such a system, and fine-tuning operating set points to minimize the life-cycle cost of the system. This would be the largest system to date for Trevi, on the path to build commercial-scale systems.

Project output was going to be a cost estimate to Orange County ratepayers for the additional water, which includes factors such as energy needed to produce this water, maximum recovery, and cleaning frequency.

To achieve these objectives, Trevi explored developing an FO membrane assembly that is resistant to fouling and scaling with low chemical consumption. This task proved to be more time-consuming than anticipated. The authors are close to achieving this goal, and it makes sense to continue at small scale for a few more months to conclude this aspect before building and operating a 100 m^3/day system.

With the project end date near and the team was without the full set of data from the continuing small and medium scale testing – it was determined it may not be possible to successfully design, build and operate the 100 m^3/day system.

The project team mutually ended the project ahead of schedule, finish the small-scale optimization, and then reapply for a future Energy Commission grant opportunities for the 100 m^3/day system.

Out of the five initial objectives of the grant, the research team determined the fouling performance of the FO membranes by monitoring the flux decline (as a percentage) in the membrane over a one-year period using the software model developed and project membrane lifetime and cleaning regime to establish baseline maintenance procedures.

The work performed to reach these objectives was performed from August 2014 through May 2017 as follows:

1. Initial laboratory work to:
    a. Select a membrane manufacturer
    b. Perform initial fouling studies
    c. Test backwash as a technique to recover
    d. Test membrane shaking as a method to delay the onset of fouling
2. Small-scale field study
    a. Tests to assess fouling for different FO membrane module geometries
    b. Pretreatment study and economic comparison
3. Medium-scale field study
    a. Study of membrane recovery versus cleaning frequency for the preferred immersed modules

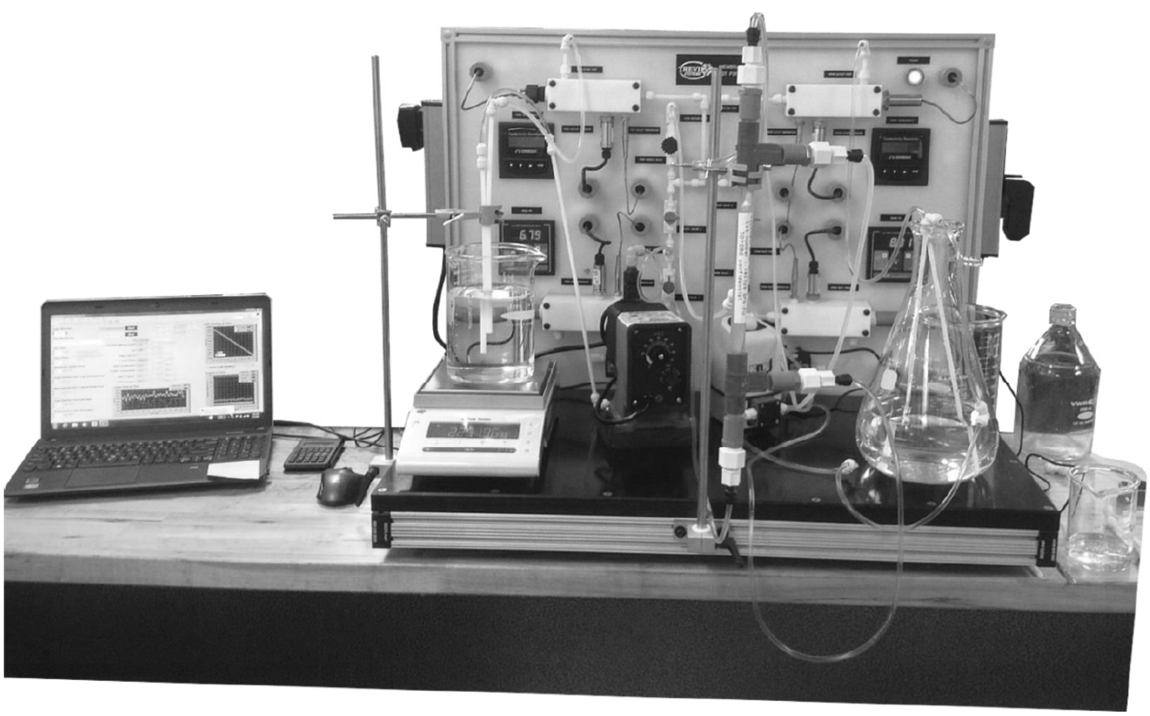
CHAPTER 2: Laboratory Work to Guide Field Work

The research team conducted laboratory work to inform the design of the field studies and related equipment. Laboratory work included the selection of a membrane manufacturer, initial fouling experiments with a synthetic Orange County Water (sOCW) of composition similar to that of the ROC at OCWD, experimentation with fouling cleaning, and prevention. Based on these studies, the team defined initial recovery targets for the field studies.

Test Setup

The research team performed all laboratory tests on a Trevi FO test setup similar to the one shown in Figure 5. The test setups measured flux based on mass difference over time. The pH, conductivity, flow rates, temperature, and pressure were automatically recorded by a LabVIEW program. The setup was designed to be operated with hollow fiber or flat-sheet modules.

Figure 5: Trevi Membrane Test Fixture (Generation I)



Source: Trevi Systems

Water Chemistry

The research team conducted all membrane performance tests with feed made with (1) distilled water, (2) salt water of similar osmotic pressure as OCWD ROC water, and (3) sOCW).The composition of OCWD's ROC is based on the following water analysis shown in Table 1 . The speciation of silica and organic matter was not known so model compounds assumed 100%silica dioxide solution and organic carbon\; an antiscalant was added to the water as well.

All fouling tests were performed with sOCW .

Table 1: Average RO Concentrate Composition at OCWD

Constituent	Detection Limit	Typical RO Brine (average)
Alkalinity-Phenolphthalein	1mg/L	-
Nitrite Nitrogen	0.002mg/L	0.93
Silica	1mg/L	121.3
Total Organic Carbon (Unfil)	0.05mg/L	29.13
Bromide	0.1mg/L	1.73
Chloride	0.5mg/L	1483.3
Nitrate Nitrogen	0.1mg/L	50.93
Sulfate	0.5mg/L	1386.7
Organic Nitrogen	0.1mg/L	2.77
Total Kjeldahl Nitrogen	0.2mg/L	5.43
Boron	0.1mg/L	0.83
Calcium	0.1mg/L	519
Chromium	1ug/L	5.73
Iron	1ug/L	625
Potassium	0.1mg/L	103.7
Magnesium	0.1mg/L	165.3
Sodium	0.1mg/L	1150
Total Hardness (as CaCO3)	1mg/L	1973.3
Silver	1ug/L	-
Aluminum	1ug/L	20.4
Arsenic	1ug/L	4.27
Barium	1ug/L	167
Beryllium	0.5ug/L	-
Cadmium	1ug/L	-
Cobalt	1ug/L	2.67
Copper	1ug/L	17.87
Gadolinium	10ng/L	1013.3
Mercury	0.1ug/L	1.17
Manganese	1ug/L	225.7
Nickel	1ug/L	37.17
Lead	1ug/L	-
Antimony	0.5ug/L	5.03
Selenium	1ug/L	11.4

Thallium	0.5ug/L	-
Vanadium	1ug/L	14.43
Zinc	1ug/L	129
Phosphate Phosphorus (orthophosphate)	0.01mg/L	4.54
Total Dissolved Solids	1mg/L	5810
Electrical Conductivity	1uS	8360
Total Alkalinity (as CaCO3)	1mg/L	1030
Hydroxide (as CaCO3)	1mg/L	-
Bicarbonate (as CaCO3)	1mg/L	1030
Carbonate (as CaCO3)	1mg/L	-
Ammonia Nitrogen	0.1mg/L	2.67
pH	7.4-7.5	

Source: Trevi System

Membrane Selection

The team compared membranes from several manufacturers based on performance under standard test conditions and on their commercial availability at the time of the project. Membranes manufacturers shown in Table 2 were considered for use in this project at the end of 2014 and early 2015. Membranes were tested for comparative performance.

Table 2: Membrane Manufacturers Considered for this Project

Manufacturer	Geometry	Commercial Availability
Toyobo	Hollow fibers	YES
HTI	Flat sheet	Stopped being available
HTI	Hollow fibers	Stopped being available
Aquaporin	Flat sheets	Still in development

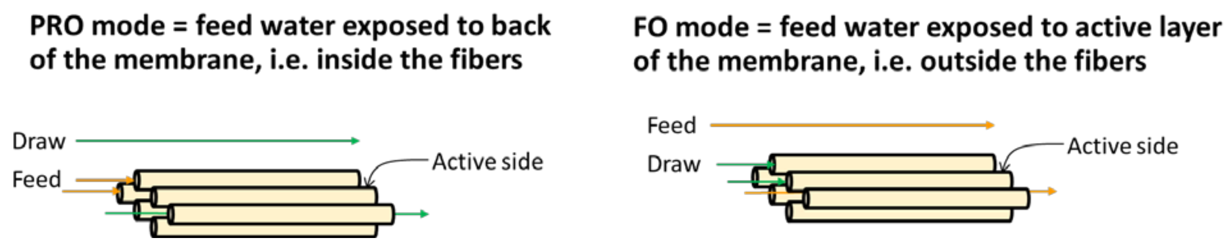
Source: Trevi Systems

Ultimately, although several membranes yielded promising performance (high flux and rejection), only Toyobo was able to guarantee the delivery of quantities necessary for the 100 m^3/day system during the project timeline. HTI was going through financial difficulties and the future of the company was uncertain.

Historically, Toyobo was manufacturing hollow fiber reverse osmosis membranes. In partnership with Trevi Systems, it expanded its membrane business to FO. The hollow fiber geometry, in which clean water is transported from the feed through the wall of a straw like membrane into the draw solution (Figure 6), is attractive because membrane flux is typically lower than for flat sheets, which could reduce fouling potential. And although flow per surface area of the membrane (= flux) is lower than for flat sheets, because more surface area can be packed per volume, the amount of water produced per element is about the same. Therefore, Toyobo membranes were used for this project.

The membranes were run in two modes: PRO mode means that the feed water was exposed to the back of the membrane and the draw was exposed to the front of the active side of the fibers, whereas FO mode means that the feed water is exposed to the active side of the membrane, with the draw exposed to the back of the fibers.

Figure 6: Hollow Fiber FO Membrane with Active Layer on the Outside and the Two Run Modes



Source: Trevi Systems

Toyobo's fibers are made of cellulose triacetate, and the active side is on the outside. Toyobo agreed to provide fibers of various diameters and lengths for research and to work toward providing modules made to the research team's design suggestions at a large scale. Laboratory measurements were performed to optimize length, diameter, and packing density. An example of data collected is shown in Table 3. Membrane flux is shown to increase with increasing diameter.

Table 3: Comparison of Flux as a Function of Fiber Internal Diameter

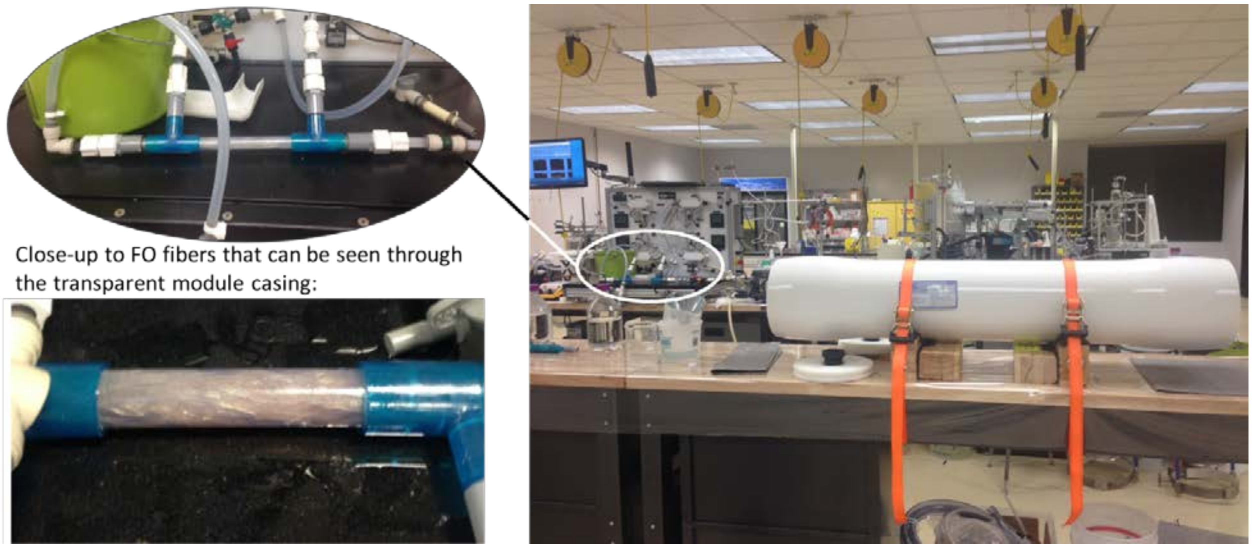
Membrane internal diameter (micrometers)	Flux (liters per minute per hour, LMH) when active layer in contact with the feed	Flux (LMH) when active layer in contact with the draw
230	0.45	3.2
430	0.65	3.9
1023	0.70	5.2

Test conditions were Trevi's proprietary draw solution against 0.6 percent sodium chloride, with feed cross flow velocity of 2 centimeters per second (cm/s) and draw cross flow velocity of 0.16 cm/s, fiber length of 8 inches, fiber packing density of 35 percent and no pressure.

Source: Trevi Systems

All reported laboratory and field tests were performed with Toyobo FO hollow fiber membranes. Toyobo provided laboratory size membrane modules of 8 inches in length and 0.8-inch diameter that typically contained 900 membrane fibers at 35% packing density. The module envelope was made of transparent plastic, which made it easy to observe fouling. A size comparison between commercial and lab size modules is shown in Figure 7. A close-up of the woven pattern is shown in Figure 8. In contrast to the commercial modules, the fibers in the small modules were not woven. This will have implications later for fouling.

Figure 7: Size Comparison of Research and Commercial Forward Osmosis Modules, and Close-Up on FO Fibers



Source: Trevi Systems

Figure 8 Woven Fibers

Source: Trevi Systems

Fouling Studies

A laboratory size module was 8 inches in length and 0.8-inch diameter and typically contained 900 membrane fibers. Commercial-size modules contain fibers that are 40 inches long. When water from the feed is transferred through the membrane to the clean side, the feed becomes more concentrated. Two major questions are what concentration causes the onset of scaling, and what the effect on membrane flux is. To mimic fouling of commercial size modules, the sOCW recipe was made at different strengths to mimic different recoveries. The minimum recovery studied was 50% because lower recoveries would not be economically meaningful. A white deposit was observed, and over time, a near-complete clogging of the module appeared.

Cleaning Experiments

The following cleaning methods were tested once the module was scaled (defined as 30% flux reduction):

- When the module was run with active layer in contact with the feed water, the feed velocity was increased to flush the scaling. This approach would not work for the dense scaling on reverse osmosis membranes, but the thought was that the fouling layer is “fluffier” in FO and that a flush with a high-velocity feed would displace the scaling out of the module. This did not happen.
- When the module was run with active layer in contact with the draw solution, the draw solution was replaced with distilled water in the hope that the reversal of osmotic flow direction would detach the scaling from the membrane and the scaling would be transported out of the module. This did not happen.
- Pressure on the distilled water (bore) side was added in the previous situation to see if that would aid detaching scaling. It did not.
- When the feed solution in the previous experiment was replaced with a solution of high osmotic pressure, (23% by weight of magnesium sulfate), cleaning was effective, and flux was recovered.

Practically this would mean the feed and draw solutions must be replaced during cleaning and a small pressure of 30 pounds per square inch (psi) of pressure must be applied to the bore side. No pH adjustment would be required, and no expensive proprietary chemicals would be purchased.

Effect of Shaking on Fouling Prevention and Commercial Implications

A small motor was attached to a laboratory-size module, and a fouling experiment was run to compare the onset and extent of fouling to an experiment where the module was not shaken. There was a delay in the onset of scaling, but ultimately, the extent of flux decline was similar. This is because the module was closed, and scaling built up from water chemistry conditions. If the module geometry was open, shaking the module might have made a difference. This was tried with success in the field at the medium scale as discussed in Chapter 5.

Conclusion and Next Steps

When feeding sOCW, fouling occurred at recoveries starting at 50%. An effective cleaning method was to switch feed and draw with a solution of high osmotic pressure and distilled water, respectively, and to add 30 psi of pressure on the bore side. This synthetic water was created by the research team to mimic the chemical composition from OCWD’s reverse osmosis process.

Although useful, laboratory experiments do not replace field fouling studies. The synthetic water chemistry was only approximating the water chemistry at OCWD. The speciation of silica and organic matter was not known. Both of these species drastically affect fouling. For this reason, fouling studies must be conducted in the field. The laboratory studies provided a start point for conditions to experiment in the field and for cleaning methods that worked.

CHAPTER 3: Small-Scale Pilot Tests at OCWD Without Pretreatment

Introduction

Two thermoresponsive FO systems were designed and built to operate at a small scale in the field at OCWD. The goal was to expose the FO membrane directly to ROC and observe fouling over time. Fouling studies can take weeks or months to complete. Two module configurations were tested: the typical enclosed module that Trevi had installed at many other test sites, and an innovative, research-size, immersed module.

Small Pilot Systems

Two small-scale FO units were designed, fabricated, and deployed under the research canopy at OCWD to perform FO of the ROC feed and regenerate in real time Trevi's thermoresponsive draw solution. Each system was designed to handle up to six small membrane mini-modules in series (equivalent to the total length of a commercial module, each system allows samples to be taken between each mini module.). Real-time regeneration of the draw solution was a new development compared to the laboratory units, allowed for continuous operation, and is necessary for long-term fouling studies (Figure 10). A LabVIEW program was written to automatically collect data. A picture of the small-scale system is shown in Figure 9.

The research team measured flux with a scale because it is more precise and accurate than flow-rate measurements. In the laboratory environment, where temperature is constant, that approach worked flawlessly. However, when the systems were placed outside, the team discovered that the density of the polymer changed a lot with temperature and that it introduced error in the flux measurements. To remediate to the situation, the team thermally insulated a portion of the system.

Figure 9: The Two Trevi Small-Scale FO Pilot Systems at OCWD

Source: Trevi Systems

Figure 10: Close Up of Trevi's Draw Solution Separators (Without Insulation)

Source: Trevi Systems

The research team performed field water chemistry analysis with the following instruments:

- Myron Ultrameter for manual conductivity and pH measurements
- HACH DR1900 spectrophotometer for calcium, magnesium, silica, sulfate, iron, etc.

Background on Fouling

The feed water for all field experiments was GWRS's ROC waste stream that contains everything that passed through microfiltration but did not pass through the RO membrane, plus an organic anti-scalant that is dosed in the RO feed. A picture of the dark brown ROC is shown in Figure 11. The compounds that do not pass through the RO membrane can accumulate at the membrane surface. When this accumulation causes a decrease in the amount of water that passes through the membrane (the flux), this accumulation is called fouling. In addition to causing flux decline, this accumulation can cause an increase in pressure in the feed channel for enclosed membrane modules. Types of foulants include microorganisms, organic matter, salts, and colloids. They are all present at OCWD. Fouling in FO is thought to be less dense and, therefore, easier to clean than in RO.

Figure 11: GWRS RO Concentrate, the Feed to the System

Exposing Enclosed Modules to ROC

In the first field experiment, ROC was fed to enclosed modules against Trevi's thermoresponsive draw solution in PRO mode to observe fouling behavior.

PRO mode (feed exposed to the back of the membrane fibers and draw to the front) was chosen because:

- The commercial-size modules are woven, meaning the fibers are crisscrossing. This is advantageous to promote mixing and to provide integrity to the module. Unfortunately, it also creates areas of low or zero velocity (when the fibers touch each other) that promote fouling through nucleation when the feed is exposed to that side. If the feed is inside the fibers, there is no area of zero velocity due to geometry.
- The flux in the PRO mode is higher, which means that fewer modules will be required, and this would decrease the capital cost of a system.
- The draw solution is more viscous than water. So when placed inside small-diameter fibers (FO mode), a higher pressure is required to maintain the same cross-flow velocity needed for proper functioning of the module compared to a fiber with a larger diameter. Pressure is added energy, which the researchers try to avoid. By having the draw on the outside of the fibers, the research team can use fibers of smaller diameter, which allows

one to pack more surface area inside the module and therefore reduce the number of modules needed, which reduces the capital cost. The fact that larger-diameter fibers have a higher flux offsets this to a certain extent (Table 3). Moreover, Toyobo guaranteed being able to produce large modules with smaller fiber diameters (230 micrometers). The large diameter fibers were produced for research, and it would take much longer to produce these fibers in large quantities. Toyobo was not sure it could produce the large-diameter fibers at commercial scale for the timeline of this project.

- However, in PRO mode, the feed water containing the fouling species is exposed to the back of the fibers, which typically have large openings. This increases the chance of internal membrane fouling. (The compounds are able to lodge inside the membrane.) Toyobo assured the research team that the back side of the membranes is very similar in size of openings as the active layer, so this should not be a great issue.

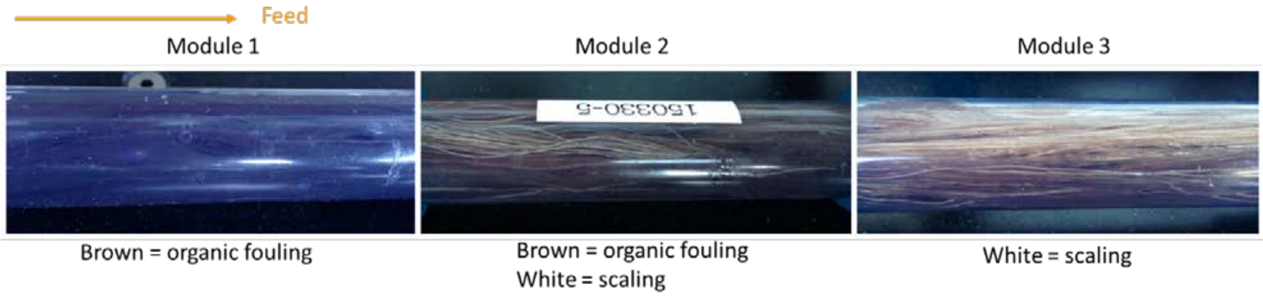
Three small modules were arranged in series to form a 24-inch long equivalent module. (The commercial-size modules are typically 40 inches long). When running in PRO mode, the research team lost 40% of the flux in 35 hours, from 2 liters per minute per hour (LMH) to 1.2 LMH. This was unacceptable. For comparison, RO cleaning occurs when 15% flux decline is observed; typical cleaning frequency is at most four times per year; often, it is only once or twice a year.

The membrane fibers are light beige when new. Since the modules are transparent, fouling could be visually observed in addition to monitoring the flux decline.

Figure 12 shows the observable fouling:

- Dark brown organic fouling in the module closest to the feed (in this image, the blue hue of the module prevents one from seeing what was observed in person)
- A transition of brown organic fouling to white salt precipitation (scaling) in the middle module
- White scaling in the last module. As water is extracted from the feed by fluxing through the membrane, the salt concentrations increase until they are so high that they precipitate. Scaling typically occurs at the later stages in RO, and the same was observed here.

Figure 12: Visual Evidence of Fouling on Membranes Exposed to ROC in PRO Mode



Source: Trevi Systems

A high-velocity water flush did not recover flux, as expected from the laboratory study. The research team did not pursue cleaning options for this configuration because it was not deemed viable (fouling too fast).

In conclusion, ROC cannot be fed to an enclosed FO module with woven hollow fibers without pretreatment.

Small-Scale Tests of a New Module Geometry

The ideal treatment scheme avoids feed pretreatment upstream of the FO membranes because it is costly and potentially requires a lot of chemicals that have to be stored on-site. An option is to change the module geometry to an immersed module (Figure 14). In an immersed module, a bunch of fibers are immersed into a feed tank, and the draw is circulated through inside the bore; there is no outside shell. This geometry must be run in FO mode (feed exposed to outside active membrane surface). Compared to the above run in PRO, wider diameters are preferred. This reduces the surface area packing density, but this is potentially offset with the higher flux. The packing density is lower, but there is no pressure buildup thereby reducing electrical energy use, and the fibers are not woven, which helps with fouling potential compared to the enclosed module.

Toyobo provided experimental small immersed modules larger than was available commercially (diameter 400 micrometers, compared to 230 micrometers), so the research team could run tests in FO mode at economically meaningful flow rates and pressures.

In this preliminary experiment, recovery was 100%. (There was no brine out; concentration was allowed to increase inside the tank, creating a self-seeding situation where the salts precipitated.) The research team ran the setup in Figure 13 for three weeks. Flux results are shown in Figure 15. The flux dropped from 0.55 LMH to 0.4 LMH in four days then continued for the next two weeks with a very small decline to 0.3 LMH. Overall, the flux decreased by 30% in three weeks, which is much better than 40% in 35 hours in the enclosed module experiment.

It may appear that the correct comparison between the two experiments should not be time, but the volume of water that passes through the membrane. The amount of water that passed through membrane in 35 hours in the enclosed module experiment roughly corresponds to the amount of water that passed in 140 hours in the second experiment. This corresponds to 30%

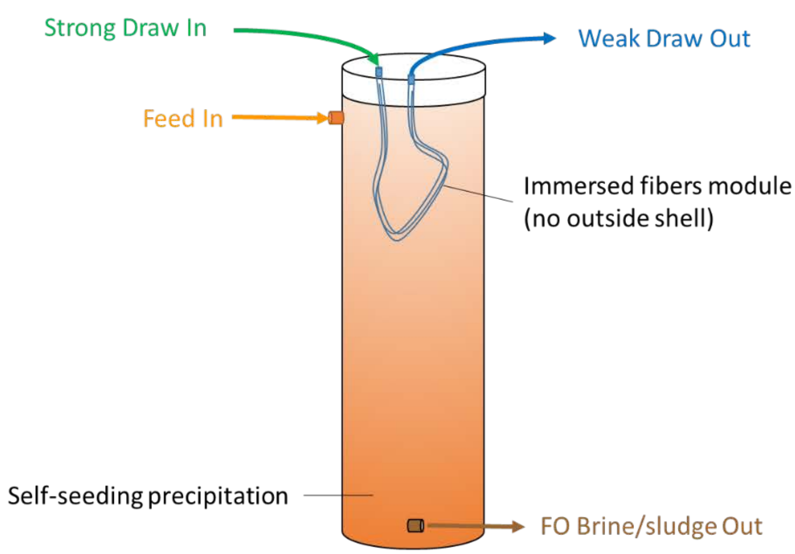
flux decline, where the flux drop levels off. However, the two experiments were run at very different recoveries, and this comparison is meaningless.

Such a flux decline would normally indicate fouling. However, since the research team operated at 100% recovery, feed osmotic pressure kept increasing due to accumulation of salts in the feed tank. The team did not measure change of osmotic pressure in this experiment but measured conductivity as a surrogate (Figure 16). Conductivity is not a perfect indicator for osmotic pressure, but an increase in conductivity is related to an increase in osmotic pressure.

The more rapid flux decline at the beginning can be attributed to the concentration of the divalent salt increasing to saturation. Upon saturation, these divalent salts start precipitating, as evidenced by the white deposit observed at the bottom of the tank. The advantage of an immersed module is that the salt precipitation is allowed to sink at the bottom of the tank instead of staying in close contact with the fibers (which was causing channel fouling and pressure increase in the feed stream in the enclosed module experiment).

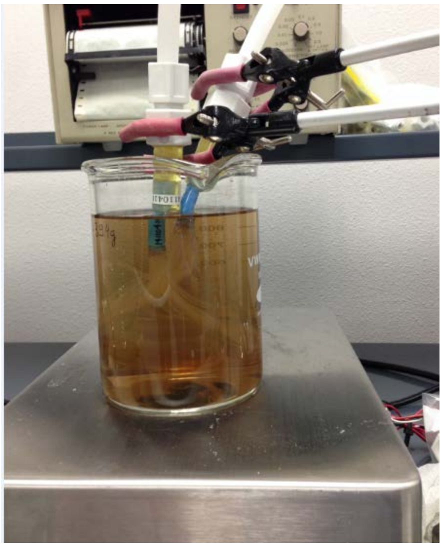
The slower flux decline afterward can be attributed to the increase in sodium chloride, which does not precipitate at the concentrations encountered.

Figure 13: Immersed Module Schematic and Photograph of Experimental Setup at OCWD



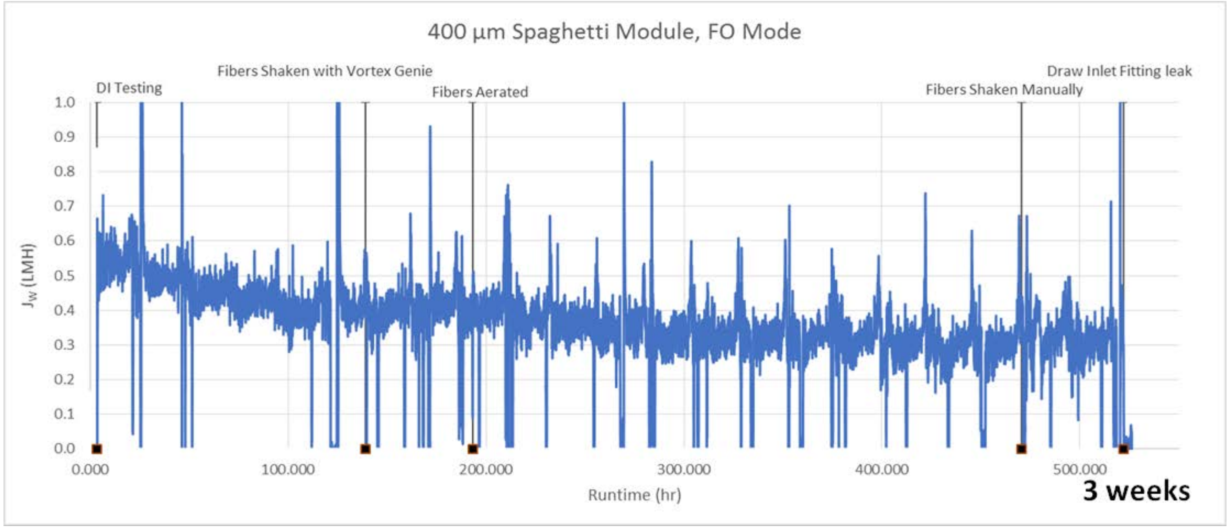
Source: Trevi Systems

Figure 14: Photograph of an Immersed Module in a Light Feed



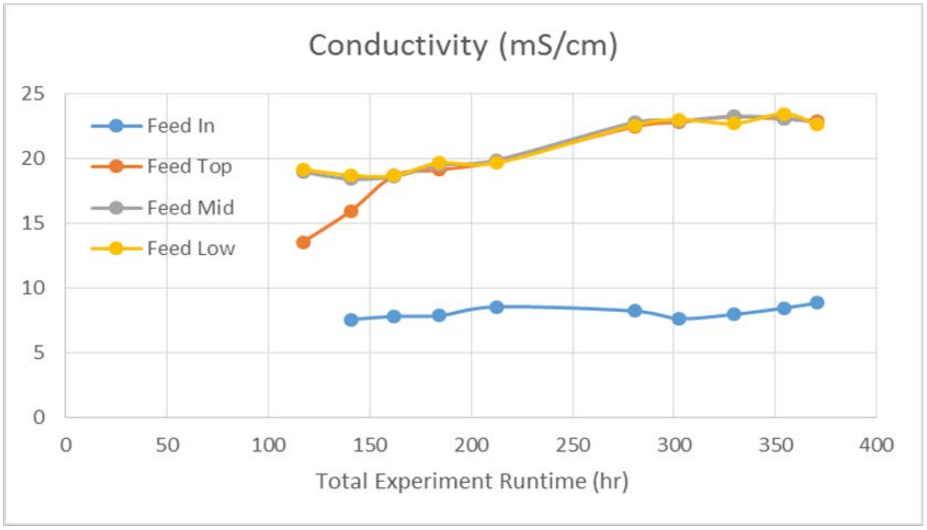
Source: Trevi Systems

Figure 15: Flux of Immersed Module When Exposed to ROC Feed Over Three Weeks



Source: Trevi Systems

Figure 16: Increase in Feed Tank Conductivity When Running at 100% Recovery for Three Weeks



Legend: Feed In = ROC entering the tank. Feed top, mid and low are conductivities measured at different tank depths. Partial data because this data was collected manually and operator was not always available.

Source: Trevi Systems

The experiment was stopped at three weeks because of a fitting leak. Nevertheless, this approach of using immersed modules appears to be much more promising than in the enclosed module. Similar data were obtained with a 230 micrometer immersed module, albeit the flux was lower and draw pressure higher (consistent with laboratory findings reported above).

Next Steps

Unfortunately, Toyobo informed the project team that it would not be able to provide immersed modules for the 100 m^3/day system within the time frame of this project because doing so requires that it scale up two innovations:

(1) Larger diameter fibers that can accommodate our draw solution in the hollow core. The manufacturer created fibers with a larger internal diameter for mini-modules but cannot make the amount of fibers required for 100 m^3/day system on its current spinning line. This has not been an issue for the research team's other projects because it has always run inside out. (The water is less challenging, fouling wise, than the OCWD ROC.) The membrane manufacturer needs to invest in a new hollow fiber spinning line.

(2) A new type of module. It weaves its fibers and rolls the "fabric" around a central tubing. The research team wants fibers that are parallel to each other akin to a typical microfiltration or ultrafiltration hollow fiber module.

During the summer of 2015, the project team had a major setback that required abandoning the enclosed modules in PRO mode because fouling was quick and severe under these conditions and pretreatment was required.

CHAPTER 4: Small-Scale Pilot Tests at OCWD With Pretreatment

Introduction

Against the setback that Toyobo would not be able to provide immersed modules for the 100 m^3/day pilot within the timeline of the project, the project team decided to test three types of pretreatment and compare the amount and types of chemicals necessary. The project team obtained feedback from OCWD on the pretreatment options.

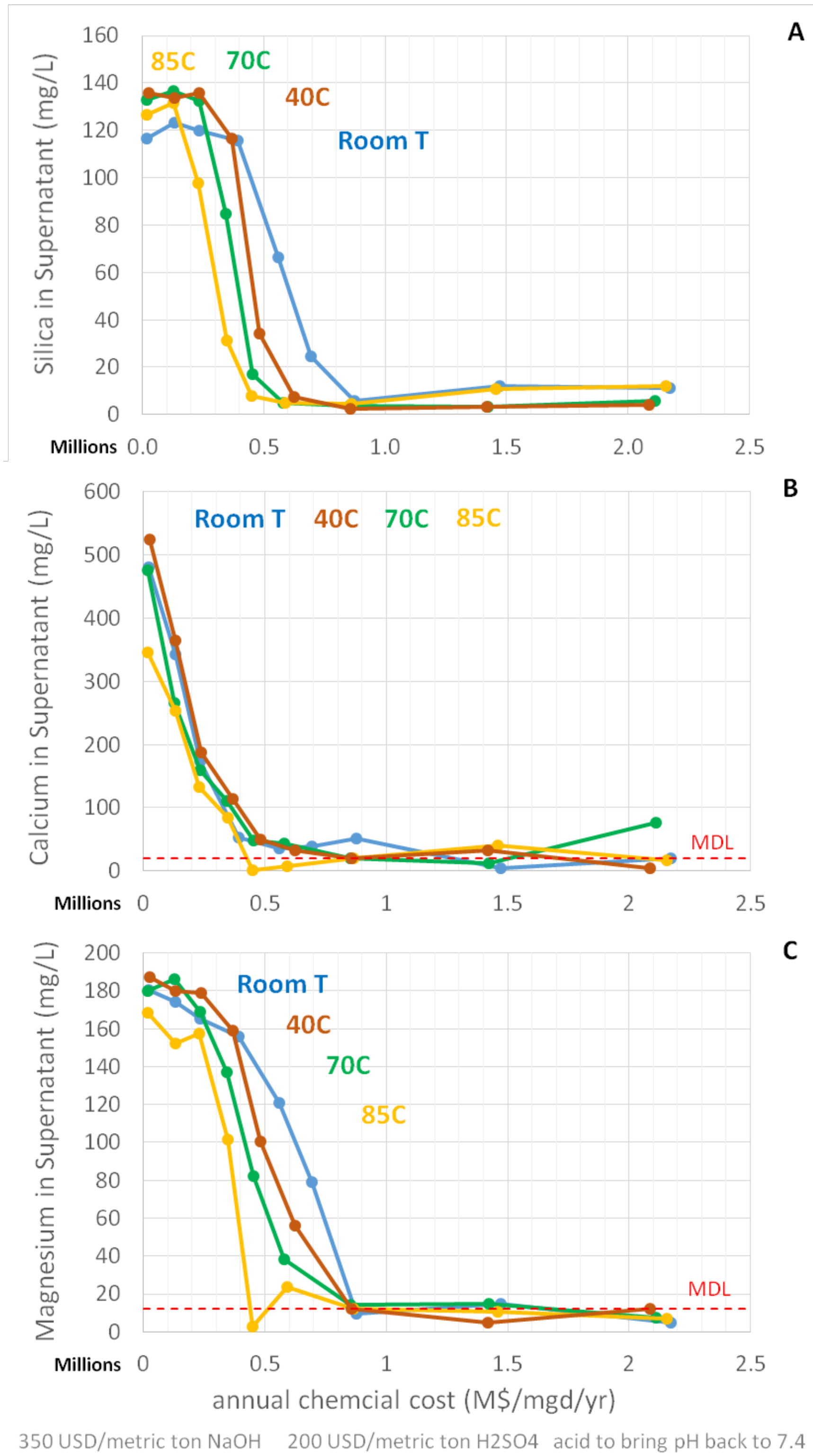
Pretreatment 1 – Chemical Softening

The first pretreatment option was to increase the pH to achieve co-precipitation of calcium, magnesium, and silica. The research team performed laboratory experiments to determine the pH needed for the precipitation of calcium, magnesium, and silica. Figure 17 shows the annual chemical cost for chemical softening treatment as a function of final concentration of silica, calcium, magnesium, and temperature (room temperature to 85 degrees Celsius). The reduction of all three species occurs simultaneously and is shown in different graphs for clarity. In all three cases, as more sodium hydroxide is dosed, a higher removal is achieved, and 90+% removals are achievable.

Because the cellulose triacetate membranes need to operate at near neutral pH (they hydrolyze at higher pH), the pH needed to be brought back down after chemical softening before sending the feed to the membranes. The higher the pH is driven up by addition of sodium hydroxide, the more acid must be added to bring the pH back to neutral, which increases the cost. The x-axis contains cost as a surrogate for amount of chemicals, in million US dollars (USD) per mgd treatment capacity per year. Cost assumptions were 350 USD/metric ton sodium chloride, 200 USD/metric ton sulfuric acid, pH adjusted back to 7.4.

Also for silica and calcium, increased temperature yielded better removal per amount of chemicals added. If waste heat is available, this is a great option to reduce the amount of chemicals that must be brought on site.

Figure 17: Annual Chemical Cost for Chemical Softening Treatment



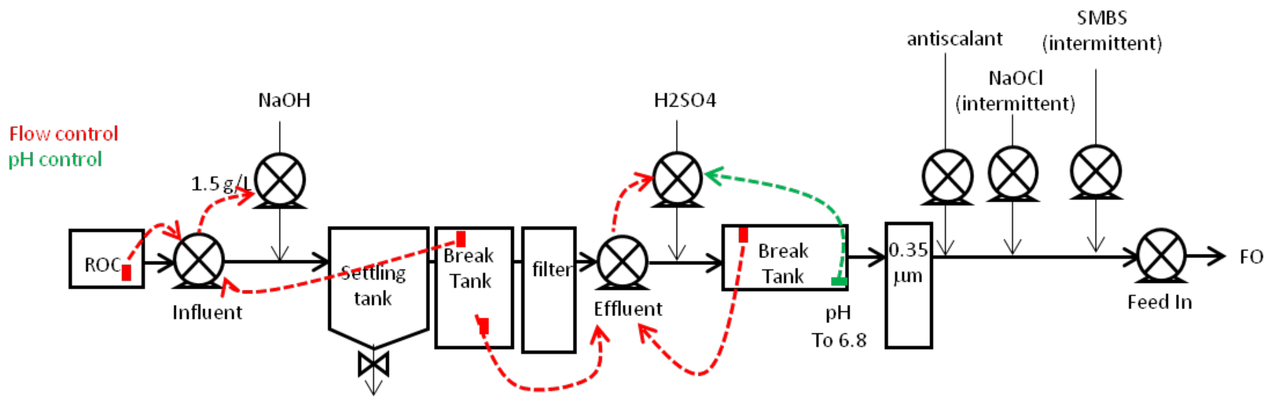
Source: Trevi Systems

Based on these laboratory results, a chemical softening treatment was designed, built, assembled, and deployed at OCWD. A Siemens controller was used to ensure that the pH always reaches neutral values before being fed to the membranes. The target pH was set at 6.8.

A schematic and a picture of the chemical softening pretreatment are shown in Figure 18 and Figure 19, respectively. Figure 19 also shows six mini-modules arranged in series on each test system. Chemical softening started with dosing sodium hydroxide to the ROC feed, which resulted in the immediate formation of flocs, or loosely aggregated particles. These flocs were allowed to settle in the settling tank. Water flowed from the top of the break tank by gravity into a break tank. Then it was dosed with sulfuric acid to reduce the pH. An ultrafilter was placed upstream of the FO membrane to protect it from potential leftover floc debris that could fall into the open settling and break tanks. An antiscalant can be dosed if necessary, since it is suspected that some of the antiscalant is removed by precipitation during pretreatment.

The addition of sodium hypochlorite and sodium metabisulfite occurs in all Trevi's FO systems irrespective of other pretreatment. Toyobo recommends dosing sodium hypochlorite (NaOCl) intermittently three times per days for one hour as a disinfectant to fight biological accumulation in the membrane modules. Sodium metabisulfite is added to remove the dissolved oxygen from the feed, to decrease degradation of the draw solution.

Figure 18: Schematic of the Chemical Softening Pretreatment



Source: Trevi Systems

It took time to optimize this pretreatment. Major challenges were:

- Optimization of the settling tank design to minimize the amount of floc traveling downstream.
- Addition of an ultrafilter to remove organics. Without it, the feed water to FO was still dark brown, and fouling was observed. A 5 or 1 micron filter still yielded fouling of the FO membranes.
- Intermittent chlorine dosage to control biofouling.

Overall, this treatment is adequate but requires a lot of chemicals, tanks, and ultrafiltration. It is a brute force approach that has been proposed in the industry.

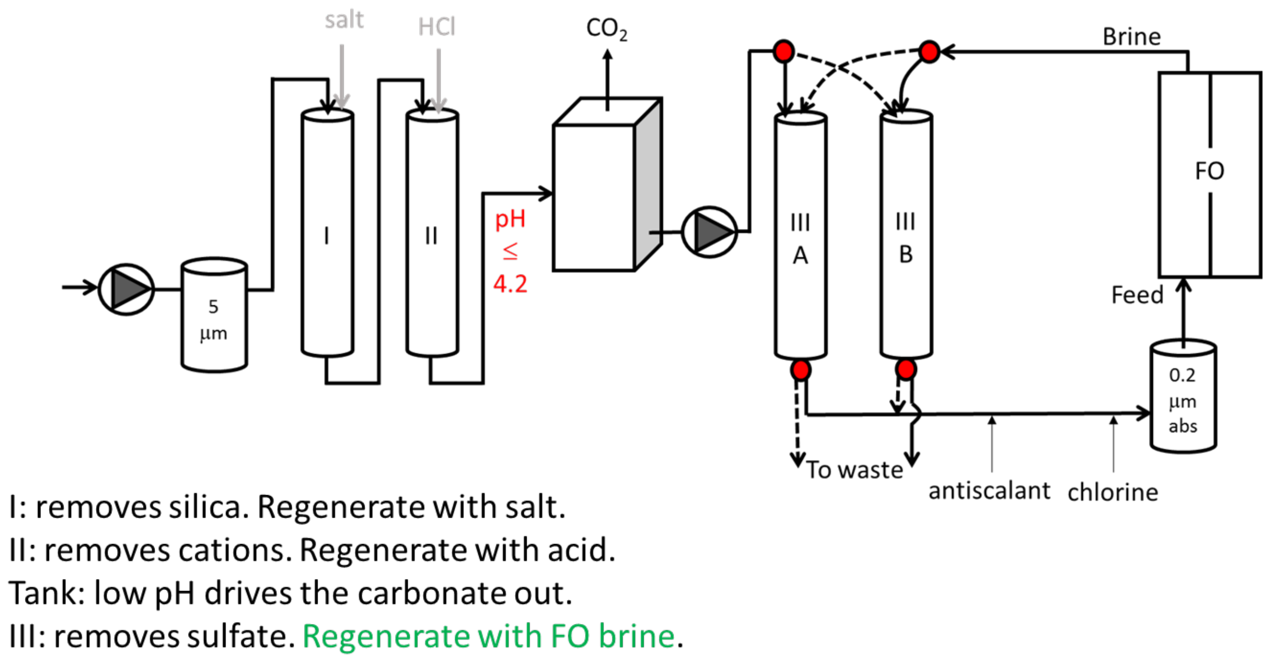
Figure 19: Picture of the Chemical Softening Pretreatment (Underneath Table) at OCWD

Source: Trevi Systems

Pretreatment 2 – Ion Exchange

Trevi Systems participated in the DesalTech conference in August 2015 and met a professor at a conference who had been developing a novel medium that removes silica very well. He proposed a treatment scheme for OCWD, seen in Figure 20, and sent the media for the three types of columns. Trevi built the treatment scheme and operated it at OCWD for several months (Figure 21). ROC was fed through a series of 1 liter columns, with a break tank between Columns II and III. Column I removes silica and can be regenerated with salt (type purposely undisclosed) when silica analysis showed increased concentration in the column effluent. Column II is a commercially available cation exchange column that can be regenerated with hydrochloric acid when the column effluent reached a pH higher than 4.2. At the exit of Column II, the pH is low, and water is fed in an open break tank. Because of the low pH, the carbonate goes out. Column III is made of a resin developed at Lehigh that removes sulfate and can be regenerated with the FO brine. The advantage is that chemicals do not need to be trucked in for regeneration of this column. However, regeneration needs to take place every four hours; therefore, two columns were needed, with switching between the two columns every four hours. This system was not automated and, therefore, was operated either four or eight hours a day, for several months.

Figure 20: The Ion Exchange Pretreatment



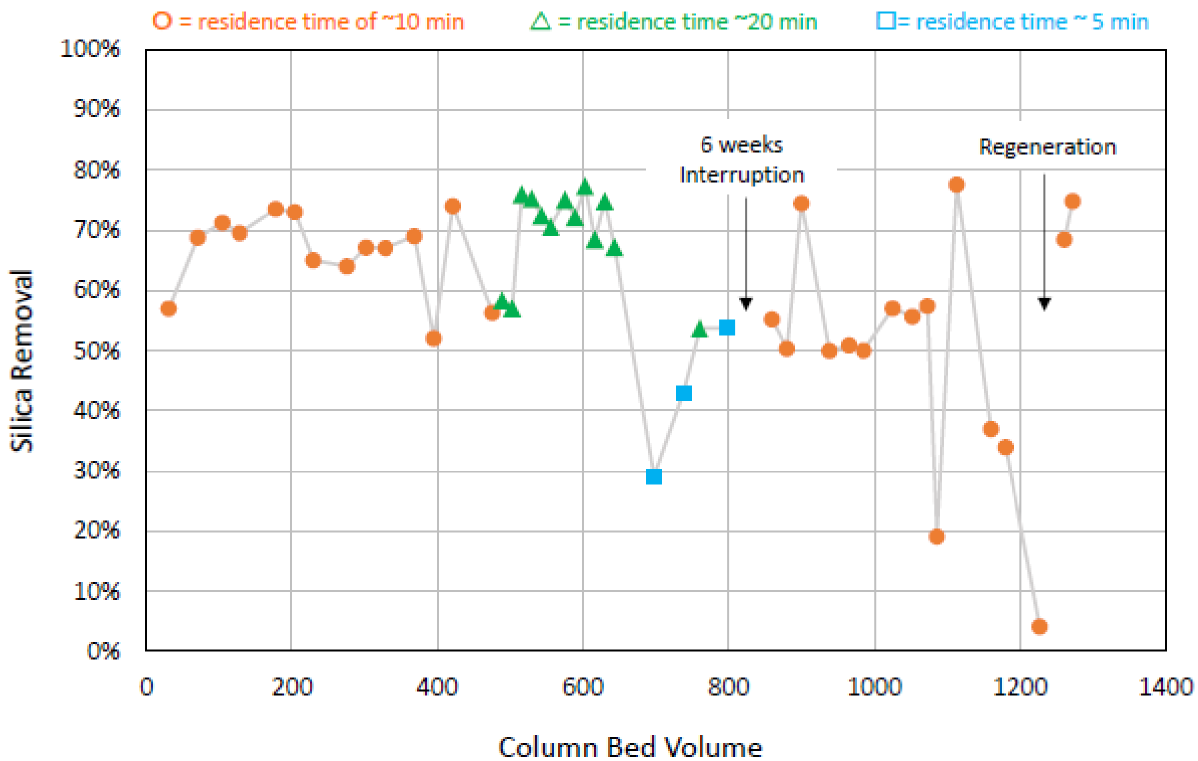
Source: Trevi Systems

Figure 21: The Ion Exchange Pretreatment (Underneath Table) at OCWD

Source: Trevi Systems

Silica removal (Figure 22) was 50%+ at residence times (or how long the fluid stays in the column) above 10 minutes for 1,000+ bed volumes when run intermittently 4-8 hours per weekday. A residence time of 5 minutes yielded poorer removals. Salt regeneration was performed at 1,220 bed volumes and yielded a recovery of the silica rejection. The field experiment ended shortly after this regeneration. The column was rinsed with deionized (DI) water and capped to keep it wet. One year later, the column was resurrected to do a lab experiment, but the column no longer rejected silica.

Figure 22: Silica Removal with Silica Sorbent at Various Residence Times

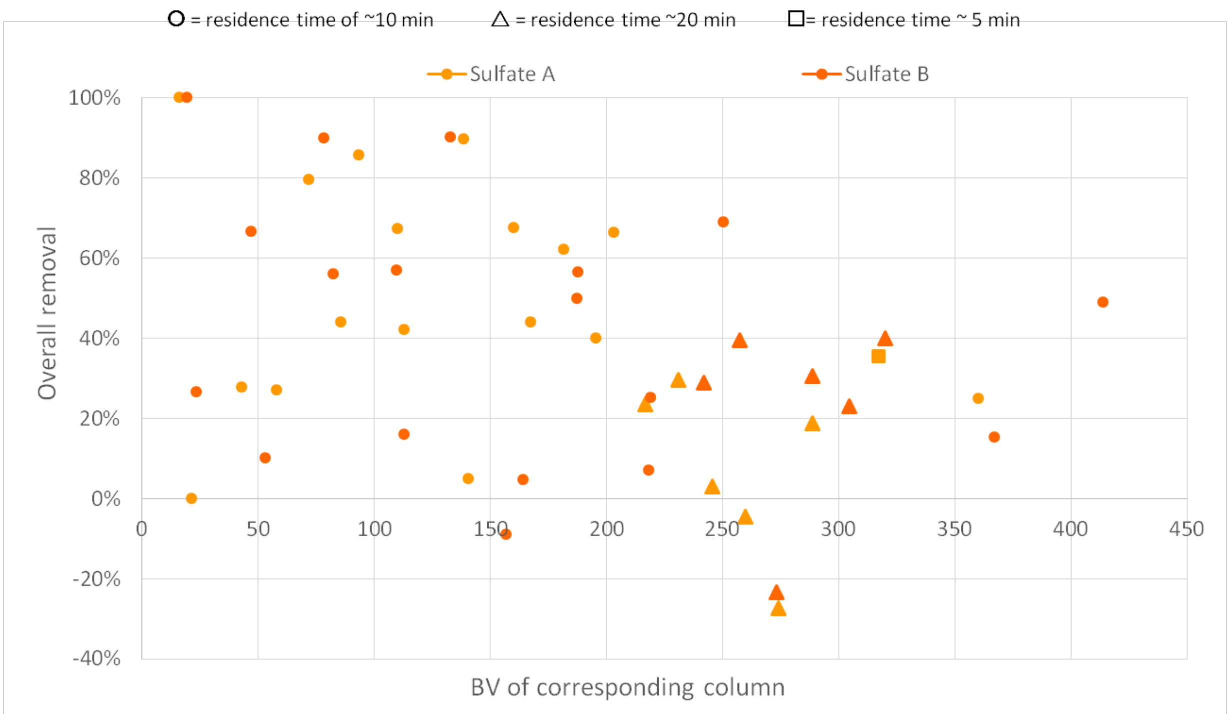


Source: Trevi Systems

Calcium and magnesium removal proved harder to assess because of chemical interferences with the test for the HACH spectrophotometer.

Carbonate removal were good, and sulfate removal (Figure 23) started high and decreased over time. One explanation for this decrease is that the FO concentrate was of lower concentration than expected because the recovery of the FO system was lower than designed. The FO recovery was low because the flow rate out of the 1liter resins was too low compared to the feed required by a small FO module.

Figure 23: Sulfate Removal with Columns IIIA and IIIB



Source: Trevi Systems

Outstanding questions include:

1. Does anything leach out of the columns that could cause fouling downstream?
2. How many times can it be regenerated, and does it recover the full performance after regeneration?
3. Can it be produced at industrial scale?
4. How much does it cost?
5. How does it compare with the new type of commercially available resin that Purolite (an ion exchange resin manufacture) is designing? (Purolite is a manufacturer of ion exchange resins which are commercially available and easier to obtain than Dr. Gupta's Lehigh resin, however, the Purolite resin was not tested during this project and performance is unknown. They are a respected company, that would make a good comparison benchmark for emerging resins).

Column II is usually not used for such high concentrations of divalent ions because it is not economically practical. However, it could be removed if the carbonate and sulfate are removed. However, to remove the carbonate, a large amount of acid would be required, which is also expensive.

Column III offers a chemical-free way to remove sulfate. Main questions include long-term performance, cost, and ability to be produced at industrial scale.

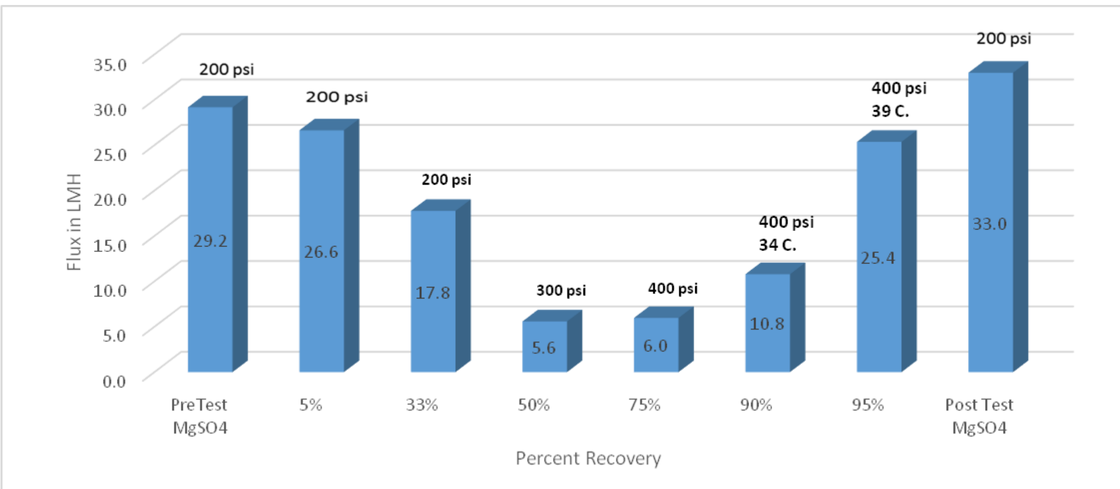
Pretreatment 3 – Self-Seeding Membranes

A nanofiltration (NF) membrane could be used to remove color and hardness with relatively low pressure and at as high a recovery as possible (the research team achieved 95+% by weight), producing a colorless, low-hardness permeate to then run through FO. The data below were collected with a setup brought to OCWD for one day to test the basic idea in a batch mode.

Flux and rejection improved with increased temperature and responded more to increase in temperature than in increase of pressure, as can be seen in Figure 24 and Figure 25.

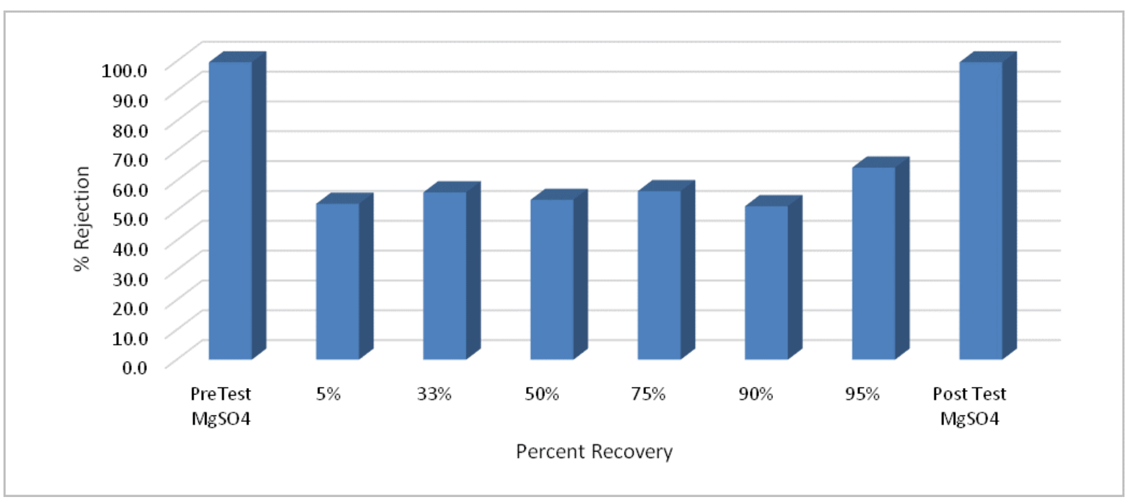
Calcium, magnesium, sulfate, and turbidity were removed (Figure 26). Carbonate was removed by 50%. Silica was only poorly removed. Organic were very well removed from visual inspection of color.

Figure 24: Nanofiltration Flux as a Function of Recovery, Pressure, and Temperature



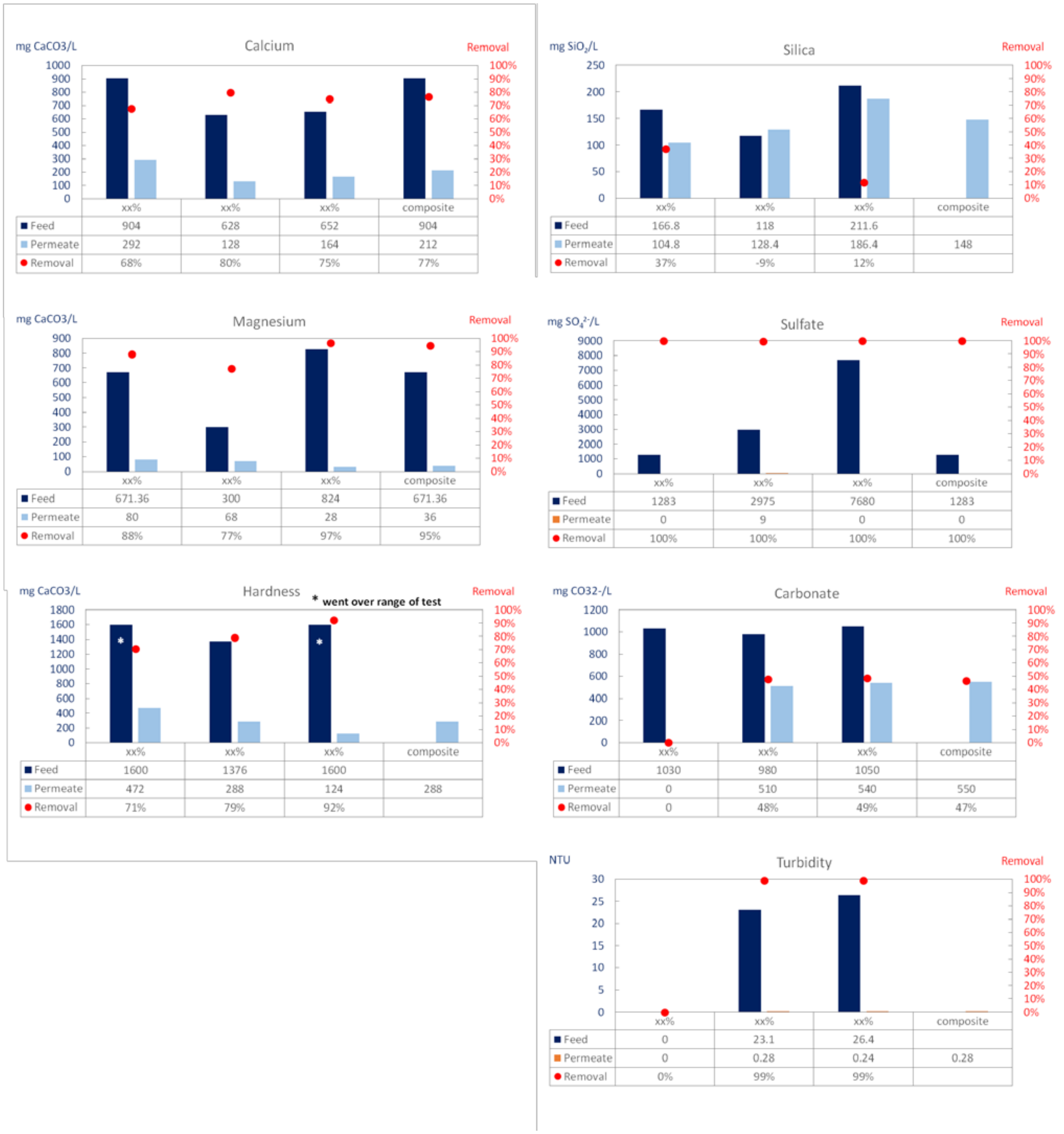
Source: Trevi Systems

Figure 25: Nanofiltration Rejection as a Function of Recovery, Pressure, and Temperature



Source: Trevi Systems

Figure 26: Nanofiltration Chemical Removal as a Function of Recovery



The next step was to design, build, and deploy a continuous system to test the fouling rate of the NF membrane. To remove silica, ion exchange could be used downstream of the NF membrane.

Comparison

A comparison of the three pretreatment options evaluation is provided in Table 4 based on the amount of chemicals necessary and corresponding number of trucks, chemical costs, and sludge that would need to be trucked out each day for a 15 mgd facility (which would treat nearly the whole GWRS current ROC produced). For this analysis, the FO target recovery was set to 90%, which is challenging and therefore required the best removal of foulants that these pretreatments could offer (maximum amount of chemicals). The feedback from OCWD staff was that all options are too expensive and require too many chemicals to be handled. Storage space and safety are concerns, as well as the number of trucks in and out of the facility since OCWD is located close to a residential area.

These pretreatments options could be used in different setting where the economics and locations are not constrained in the same manner. For example, NF membranes could be combined with a silica removal ion exchange resin.

All these pretreatments could in theory be followed by reverse osmosis instead of FO. Several companies have already created such processes. However, Trevi's FO should yield higher recoveries and lower fouling, as well as a potential energy advantage. The hope is that the chemical dose could be optimized to a lower setting for FO. A side-by-side pilot comparison between FO and RO would be needed to answer this question.

Implications for the Project and New Direction

Based on the feedback from OCWD, no chemical pretreatment is acceptable. Luckily, Toyobo made progress on the immersed module front. It was able to produce a 3inch-diameter immersed module, which is a size at which the research team could run a 100 m^3/day pilot, and it would be able to deliver enough modules for the 100 m^3/day pilot. However, the fiber diameter would be small (future products could differ, see Next Steps). Because of the small internal diameter of the fibers, the length of the fibers (there is a minimum length to be economically feasible since the potting of the fibers is expensive), and that the Trevi draw is more viscous than water, the only option was to switch the draw solution to a salt solution for this part of the project. Because it was a new type of module and Toyobo would need time to assemble the modules, a medium-scale system was designed, built, and used to experiment with up to four of the 3-inch-diameter modules. If the results of the medium-scale are good, the plan was to build the 100 m^3/day pilot on time to run six months in the field at a set point determined by the medium-scale system. Both the medium-scale and large-scale systems would be run in parallel.

Table 4: Comparison of Pretreatment Methods by Chemical Mass and Cost, and Sludge Production for a 15 mgd Facility

Pretreatment	Chemicals required for 15 mgd system	Chemical cost (million $/year)	Chemical cost (cent/1000 gallon)	# tucks of chemicals per day	Sludge production (trucks/day)	Notes
Chemical softening	1500ppm caustic soda = 25,000 gpd liquid or 96 tons/day	12.4	2.3	3	4	This does not include acid addition to bring pH back down
Ion exchange	Hydrochloric acid = 150,000 gpd liquid or 650 tons/day	47.5	8.7	18	None	May need to neutralize regeneration liquid before sending to OCSD
Seeded NF	Sulfuric acid may = 14,500 gpd or 100 tons per day	9.8	1.8	3	4	

Source: Trevi Systems

CHAPTER 5: Medium-Scale Tests of Immersed Modules

Introduction

A medium-scale test setup was designed, fabricated, and deployed at OCWD to test a full-size immersed module with a salt draw solution. (See previous page for context.) The goals were to:

- Test this module for a few months and ensure the encouraging trends observed at small scale were reproducible with a large-diameter module and over longer periods.
- Test control strategy to inform the design of the 100 m^3/day system.
- Test fouling prevention strategies and cleaning.
- Optimize recovery and cleaning frequency.

One advantage of salt draw is that the flux can be controlled independently from the recovery: changing the draw concentration changes the flux, while the recovery can be changed by changing the flow rate of the waste stream out of the feed tank. This is helpful to assist with target flux for the membrane design. The range of osmotic pressures tested was similar and lower than that of the thermoresponsive draw solution.

Design, Fabrication, and Deployment

The project team designed, fabricated, and programmed in house a system that allows running experiments with full-scale modules (Figure 27). The system is controlled automatically and plots data in real time. It also collects data automatically for further processing. Because the draw was a salt draw, the separation became a reverse osmosis system instead of Trevi's thermal separation system. Design challenges included materials suited for very high salt concentrations on the draw side and provisions for easy cleaning for the high fouling feed side.

Features of the system include:

- In-house program to control and show data in real time and collect them in text files.
- Cabinetry that hides all instruments and pipes to aesthetics and promotes easy cleaning in case of spills.
- 80/20 framing (a standard T-framing system commercially available) and that offers provided assembly freedom. The coated aluminum resisted salt corrosion for the seven-month duration of the project. Screws that come with the 80/20 gear were switched to 316 stainless steel ones; the 80/20 nuts will rust over time.

A suggestion for others wanting to build a small system is to invest in a custom-made Teflon manifold for all the probes. This will save a lot of piping space.

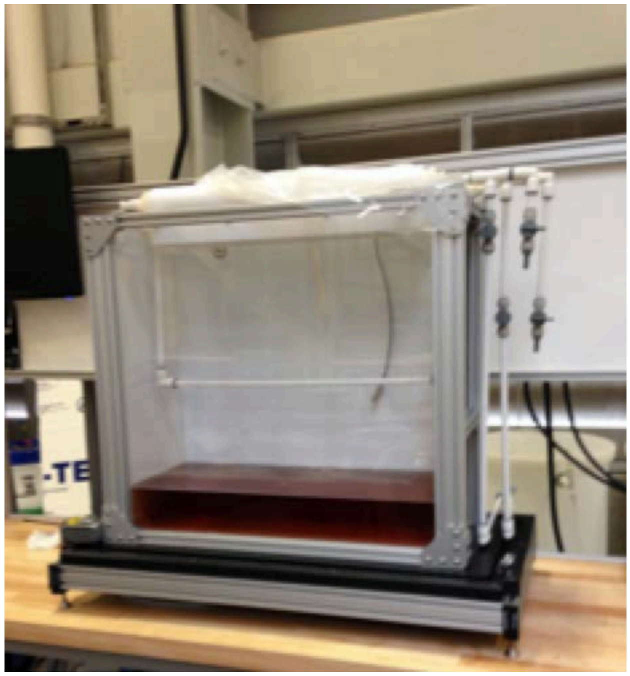
The system was tested in the laboratory and then trucked to OCWD.

Figure 27: Medium-Scale System with Feed Tank Full of ROC

The medium-scale system can handle the flows of two full-scale modules in a semicircle (u-shape) and is pictured here with the feed tank full of ROC (dark brown).

Source: Trevi Systems

Figure 28: Feed Tank with Air Sparging Tube



Source: Trevi Systems

Results

After commission at low recovery, the first few experiments were run with a series of 10 mini-modules to optimize a few parameters before using the 3-inch module.

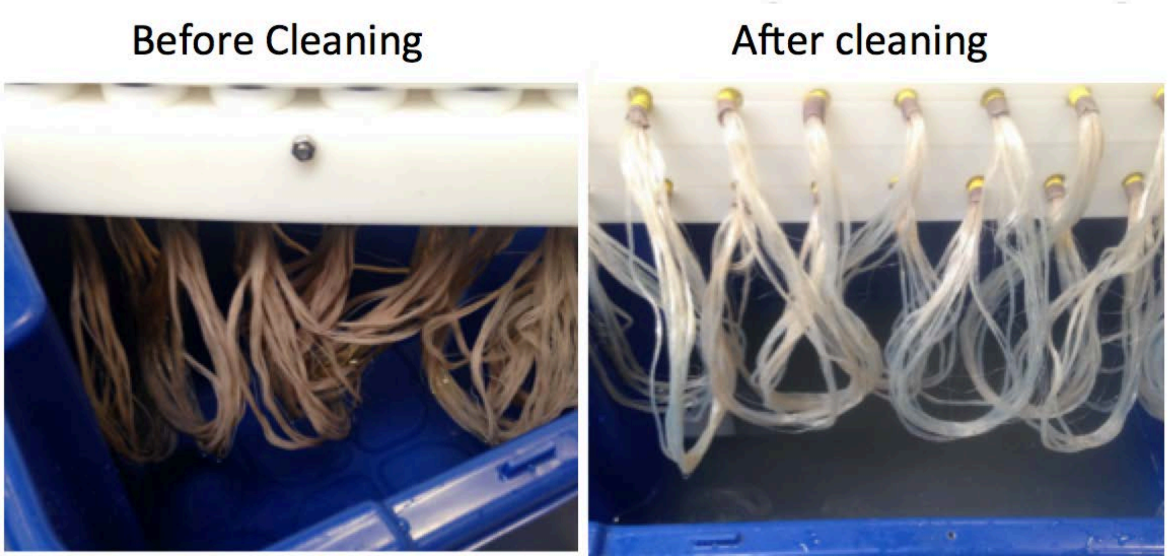
Cleaning Method

An experiment was run with small modules at 4% sodium chloride draw and 50% recovery and fouled quickly at two weeks (Figure 29). Cleaning as per membrane manufacturer recommendation with 2wt% citric acid solution adjusted to pH 4 with ammonium hydroxide allowed for recovery of the original flux and resulted in the same fouling rate afterward (i.e. fouling did not occur faster after that cleaning).

Cleaning by soaking the module in a 7% or 9 % sodium chloride solution while circulating product water in the bore also resulted in a return to initial flux. The cleaning method here is referred to as *back flush* and reverts the direction of water flux through the membrane (strong osmotic pressure salt solution on the feed side and pure water on the bore or draw side). This mechanically detaches the fouling layer. The advantage of this approach could be that the salt solution can be reused between cleaning or for many membrane modules. At full scale, one could imagine that the modules that require cleaning are automatically lifted from the immersed tank into a salt tank that can be reused (scaling would fall at the bottom of the salt tank). The salt concentration should be optimized in future work.

Both cleaning methods work, and an economic analysis will decide between them.

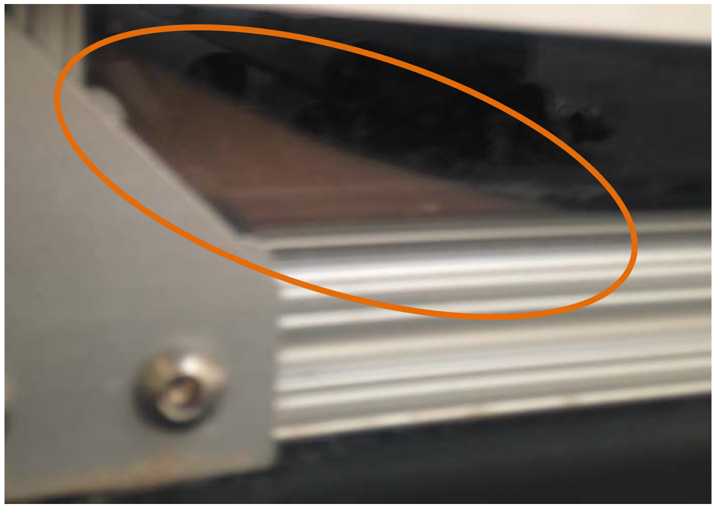
Figure 29: Membrane Fibers Before and After Cleaning With Citric Acid



Source: Trevi Systems

As observed in the first immersed membrane experiment (Chapter 3), there is evidence of scaling falling to the bottom of the tank (Figure 30). The immersed module allows for the scaling that forms to gravitate away from the membrane.

Figure 30: Evidence of Scaling at the Bottom of the Feed Tank



Source: Trevi Systems

Air Bubbling

The addition of air bubbles to move the membranes decreased cleaning frequency (Figure 28). The air bubbling regimen had to balance the minimization of cleaning frequency with the maintenance of a neutral pH. If too much air was introduced, the pH of the feed would increase to above 8, and that would shorten the lifetime of the cellulose triacetate membranes because it would accelerate the rate of hydrolysis of the polymer. Air bubbling frequency and duration were tweaked to 1 minute bubbling every five minutes. Air bubbling was performed midtank to allow salts to settle undisturbed at the bottom of the tank and to minimize air bubbling energy.

Repeating the experiment above, the duration between cleaning cycles doubled, which was encouraging.

The observation that fibers (for the small and the 3-inch module) would float with air bubbling when the membranes were clean, and would gradually sink as they were getting heavier with scaling and fouling, could be used to automate the cleaning.

Recovery Versus Cleaning Frequency

All further experiments were performed on the 3-inch (full-size) module (Figure 31) with a 4wt% sodium chloride draw and an air bubbling regimen of one minute every five minutes. Several experiments were run to compare recovery with time to cleaning, as shown in Table 5.

Table 5: Recovery and Cleaning Frequency of Immersed Modules

Recovery	Flux LMH	Cleaning Frequency
50%	1.1	>4 weeks
60%	0.9	4 weeks
70%	0.7	> 2 weeks

Source: Trevi Systems

Figure 31 The 3-Inch Modular Taken Out of the Feed Tank for Cleaning

Source: Trevi Systems

The new module design allowed for operation without any pretreatment – a very positive finding and a major benefit to any full-scale project. Data were collected to examine the tradeoff between membrane recovery and cleaning frequency. In other words, achieving higher recoveries increased fouling and, therefore, required more cleaning. Cleaning includes a salt solution (no harsh chemicals) and could be automated like a microfiltration unit (at OCWD the microfiltration unit must be cleaned every three weeks)

Membrane Autopsy

Avista performed an autopsy of a small module to determine the nature of the fouling material. The fouled fibers had an uneven coating of a beige granular fouling material. Some tests were conducted on the foulant material that was removed from the fibers during drying (necessary for some of the analyses), and other tests were performed both on the foulant removed from the fibers and on the fibers. Loss on ignition test of detached foulant material revealed fouling was mostly inorganic (~80%). The exposure of the detached fouling material to dilute hydrochloric acid resulted in effervescence, which indicates the presence of carbonate. Fourier transform infrared (FT-IR) spectroscopy of the fouled fibers further confirmed the presence of calcium carbonate and showed that the fouling layer was thick, as indicated by the lack of detection of the peaks of the unfouled membrane fibers.

Energy dispersive X-ray (EDX) analysis showed that most of the foulant that remained on the feed side of the fibers was made of silica, and that the bulk of the foulant that detached from the fibers was calcium carbonate.

Scanning electron microscopy (SEM) imaging of the fibers showed a granular foulant material coating the bulk of the fibers, with some smooth crystalline material embedded in it. The remainder foulant was amorphous. Chromatic Elemental Imaging (CEI) (Figure 32) identified the granular material as silica and the crystalline structures as calcium carbonate. The calcium carbonate was embedded in the granular material and in the membrane fiber itself.

Based on the foulant analysis, the bulk of the foulant was composed of calcium carbonate with amounts of silica.

Next Steps

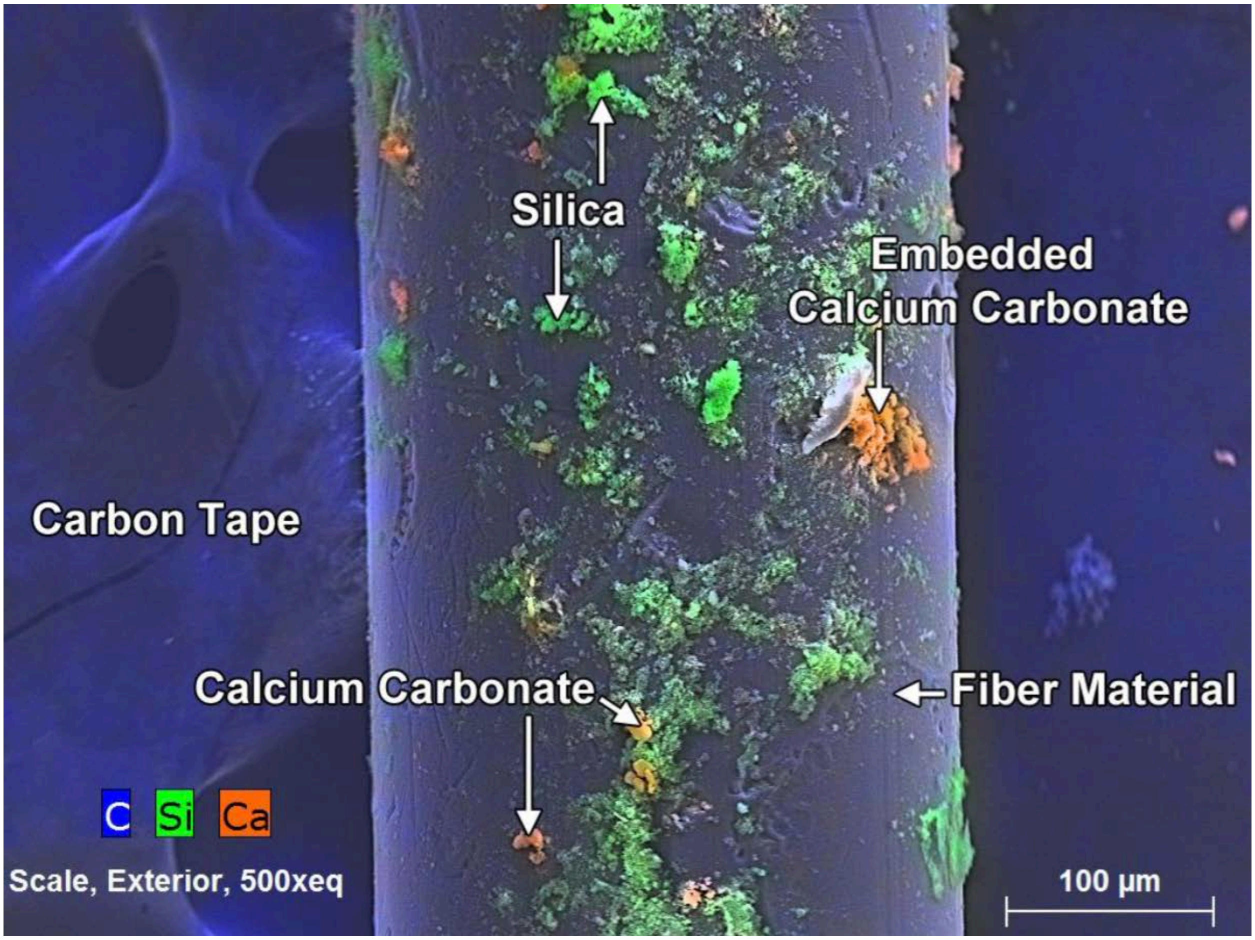
Although the results are encouraging, a major issue prevented the construction of the 100 m^3/day system within the time frame of this project. The thin cellulose triacetate fibers break easily. This was never an issue when using the commercial enclosed modules because the fibers are woven and rolled around a central tube to provide structural integrity.

At a small scale, to gather data, the project team could accommodate periodic fiber breakage. Broken modules would be replaced, and instruments on the draw side would be cleaned. (They were not designed to be exposed to feed water compounds that build deposits.) However, it would not be practical to go to a larger scale, including piloting at full scale, with these fragile membranes.

At this stage of the project, there were no other commercially available membranes at prices that made economic sense.

Parallel to this grant, Trevi Systems has been developing its own hollow fibers membranes from a material that renders them very strong, and pH and chlorine-resistant. These new hollow fiber membranes appear promising, and the research team needs to put them in an immersed module form. Afterward, the team plans to test the new membrane modules in its laboratory before testing them in the field. OCWD will consider hosting Trevi Systems again. After successful test at small scale, the research team plans to build a 100 m^3/day system

Figure 32 Chromatic Elemental Imaging (CEI) of the Foulant on a Membrane Fiber



Source: Travi Systems

CHAPTER 6: Path to Commercialization

The path to commercializing Trevi System's FO technology for RO concentrate application is:

1. Finish developing Trevi's FO membranes. Because the fibers will be of larger diameter, Trevi's system proprietary draw solution can be used.
2. Test at small scale for flux, mechanical strength, pH, oxidant, and temperature resistance, as well as aging.
3. Assemble the fibers into an immersed module of commercial scale. (The research team's pilot fiber line can output enough fiber for a small commercial laboratory in the later part of 2017.)
4. Test the module in the laboratory using the medium scale system.
5. Redeploy the medium scale system in the field (potentially at OCWD) to test fouling (study recovery compared to cleaning frequency, optimum air bubbling, and cleaning regimen). The system must be updated to use Trevi's draw solution.
6. Test module held in u-shape or straight. This will influence the economics by changing the height and width of the feed tank.
7. Perform economic analysis to optimize cleaning type and frequency, air bubbling, recovery based on data collected in this project.
8. Demonstrate that the final water quality is as good (or better) than water obtained through RO.
9. Demonstrate significant advantages of our technology over alternatives (cost or otherwise, such as less electricity used).
10. Adapt the system for easy operation.

Further concentration of the ROC questions the fate of the final brine produced by the GWRS. It would be a lot more concentrated and have the potential to clog the return pipes to OCSD. Composition of the final discharge to the ocean will change and must be compared to current and future regulations.

CHAPTER 7: Conclusions

Trevi ran FO pilots at OCWD for 2.5 years with various types of membrane modules and pretreatment. To operate on ROC feed without pretreatment, an immersed FO membrane module geometry is necessary. Results are promising, but the fibers used in this project were too fragile. Trevi is making stronger fibers, and will take longer before they can do a field trial.

Scaling up a technology is far from being linear. The reality is that crucial parts of a new system are not always available at commercial scale, and it takes time to develop these parts. In this project, developing a new hollow fiber membrane module with a willing, experienced, partner took longer than anticipated.

GLOSSARY

Term	Definition
CEI	Chromatic elemental imaging.
cm/s	Cubic meters per second. A unit of flow.
DI	De-ionized.
EDX	Energy-dispersive X-ray.
EPIC	Electric Program Investment Charge
FO	Forward osmosis. An osmotic process that uses a membrane permeable to water only to separate water from dissolved solutes. The driving force for this separation is an osmotic pressure gradient between a solution of high concentration, often referred to as a “draw” and a solution of lower concentration, referred to as the “feed”.
FT-IR	Fourier transform infrared.
GWRS	Groundwater replenishment system. An advanced water purification facility operated by the Orange County Water District that treats secondary treated wastewater with microfiltration, reverse osmosis and advanced oxidation for groundwater supply augmentation.
L	Liter. A unit of volume.
LMH	Liters per minute per hour. A unit of flux that is the amount of water that crosses a membrane per unit time and surface area.
m^3/day	Cubic meters per day. A unit of flow rate
mgd	Million gallons per day. A unit of flow rate.
NaOCl	Sodium hypochlorite.
NF	Nanofiltration.
OCWD	Orange County Water District. The field test site for this project.
psi	Pounds per square inch. A unit of pressure.

RO	Reverse osmosis. Water filtration technique that uses high-pressure pumps to force water across semi-permeable membranes.
ROC	Reverse osmosis concentrate. A liquid stream from the RO process that carries salts and organics removed from the RO feed water.
SEM	Scanning electron microscope.
sOCW	Synthetic Orange County water.
wt%	Percentage by weight.
UF	Ultrafiltration
USD	United States dollar.